



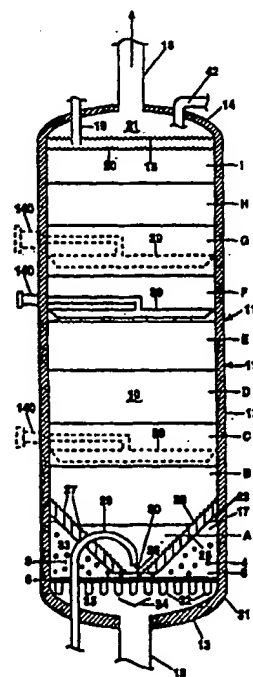
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C10G 11/18, 35/14		A1	(11) International Publication Number: WO 95/29970
			(43) International Publication Date: 9 November 1995 (09.11.95)
(21) International Application Number: PCT/US95/05280		(72) Inventors: BACHTEL, Robert, W.; 5480 Barrett Avenue, El Cerrito, CA 94530 (US). DARSOW, Brian, A.; 3715 Road Island Avenue South, St. Lewis Park, MN 55426 (US). EARLS, David, E.; 2504 Simas Avenue, Pinole, CA 94564 (US). JOHNSON, David, R.; 7 Azalea Court, Petaluma, CA 94954 (US). KLETT, Robert, J.; 3632 Fillmore Street, San Francisco, CA 94123-1602 (US). KRAMER, David, C.; 54 Brookside Drive, San Anselmo, CA 94960 (US). REYNOLDS, Bruce, E.; 1739 Jeanne Circle, Martinez, CA 94553 (US). SCHEUERMAN, Georgianna, L.; 1155 Sanders Drive, Moraga, CA 94556 (US). TRIMBLE, Harold, J.; 40 Circe Court, Novato, CA 94945 (US). BROSSARD, David, N.; 934 Warfield Avenue, Oakland, CA 94610 (US).	
(22) International Filing Date: 27 April 1995 (27.04.95)		(74) Agents: KLAASSEN, Alan, W.; Chevron Corporation Law Dept., P.O. Box 7141, San Francisco, CA 94120-7141 (US) et al.	
(30) Priority Data: 08/235,043 29 April 1994 (29.04.94) US 08/235,777 29 April 1994 (29.04.94) US 08/273,526 11 July 1994 (11.07.94) US 08/342,527 21 November 1994 (21.11.94) US		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TT, UA, UG, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).	
(71) Applicant: CHEVRON U.S.A. INC. [US/US]; P.O. Box 7141, San Francisco, CA 94120-7141 (US).		Published With international search report.	

(54) Title: CATALYST, METHOD AND APPARATUS FOR A PARTICLE REPLACEMENT SYSTEM FOR COUNTERCURRENT FEED-PACKED BED CONTACT

(57) Abstract

This invention makes possible substantially continuous flow of uniformly distributed hydrogen and hydrocarbon liquid across a densely packed catalyst bed (10) to fill substantially the entire volume of the reactor (11) by introducing the liquid and gas as alternate annular rings at a rate insufficient to ebullate the bed. Catalysts are selected by density, size and shape at a design maximum feed rate of fluids to prevent the ebullation of packed bed. The alternate annular rings flow across the full area of the bed. The catalyst flow in a continuous, downward plug-like manner is achieved by the introduction of the catalyst at the top of the bed in a laminarly flowing liquid on a periodic or semicontinuous basis. Catalyst removal is also achieved by laminar flow in the same fashion from the bottom. The catalyst used produces a plug-flowing, substantially packed bed.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

CATALYST, METHOD AND APPARATUS FOR A PARTICLE REPLACEMENT SYSTEM FOR COUNTERCURRENT FEED-PACKED BED CONTACT

5

Background of the Invention

1. Field of the Invention

The present invention relates to a catalyst and to an on-stream catalyst replacement during hydroprocessing of a hydrocarbon feed stream.

More particularly, it relates to a catalyst, a method of, and apparatus for, economically utilizing space within a hydroprocessing vessel over a wide range of processing rates without substantial fluidization or ebullition of a packed bed of catalyst during high counterflow rates of the hydrocarbon feed and a hydrogen containing gas through the packed bed, while maintaining continuous or intermittent replacement of catalyst for plug-like flow of the bed through the vessel.

20

2. Description of the Prior Art

Hydroprocessing or hydrotreatment to remove undesirable components from hydrocarbon feed streams is a well known method of catalytically treating such heavy hydrocarbons to increase their commercial value. "Heavy" hydrocarbon liquid streams, and particularly reduced crude oils, petroleum residua, tar sand bitumen, shale oil or liquified coal or reclaimed oil, generally contain product contaminants, such as sulfur, and/or nitrogen, metals and organo-metallic compounds which tend to deactivate catalyst particles during contact by the feed stream and hydrogen under hydroprocessing conditions. Such hydroprocessing conditions are normally in the range of 212 degree(s) F to 1200 degree(s) F (100 degree(s) to 650 degree(s) C.) at pressures of from 20 to 300 atmospheres. Generally such hydroprocessing is in the presence of catalyst containing group VI or VIII metals

35

-2-

such as platinum, molybdenum, tungsten, nickel, cobalt, etc., in combination with various other metallic element particles of alumina, silica, magnesia and so forth having a high surface to volume ratio. More specifically, catalyst utilized for hydrodemetallation, hydrodesulfurization, hydrodenitrification, hydrocracking etc., of heavy oils and the like are generally made up of a carrier or base material; such as alumina, silica, silica-alumina, or possibly, crystalline aluminosilicate, with one more promoter(s) or catalytically active metal(s) (or compound(s)) plus trace materials. Typical catalytically active metals utilized are cobalt, molybdenum, nickel and tungsten; however, other metals or compounds could be selected dependent on the application.

U.S. patent No. 5,076,908 to Stangeland et al provides a system wherein plug flow of the catalyst bed is maintained over a wide range of counterflow rates of a hydrocarbon feed stream and hydrogen gas throughout the volume of the substantially packed catalyst bed. Such packed bed flow maintains substantially maximum volume and density of catalyst within a given vessel's design volume by controlling the size, shape and density of the catalyst so that the bed is not substantially expanded at the design rate of fluid flow therethrough. The proper size, shape and density are determined by applying coefficients gained during extensive studying of bed expansion in a large pilot plant runs with hydrocarbon, hydrogen and catalyst at the design pressures and flow velocities as particularly described below.

To further control such packed bed flow, the bed level of catalyst within the vessel is continuously measured, as by gamma ray absorption, to assure that little ebullation of the bed is occurring. Such control is further promoted by evenly distributing both the hydrogen and liquid feed throughout the length of the bed by concentrically distributing both the hydrogen gas component and the hydrocarbon fluid feed component in

-3-

alternate, concentric annular paths across the full horizontal cross-sectional area of the vessel as they both enter the catalyst bed. Additionally, and as desirable, hydrogen is evenly redistributed and if
5 needed, augmented, through a quench system at one or more intermediate levels along the length of the catalyst bed. Equalizing hydrogen and liquid feed across the full horizontal area along the length of the packed particle bed prevents local turbulence and undesirable vertical
10 segregation of lighter particles from heavier particles flowing in a plug-like manner downwardly through the vessel.

Summary of the Invention

15 In a preferred embodiment of the invention, the present invention accomplishes its desired objects by broadly providing a catalyst comprising a plurality of catalytic particulates having a mean diameter ranging
20 from about 35 Tyler mesh to about 3 Tyler mesh; and a size distribution such that at least about 90% by weight of the catalytic particulates have a diameter ranging from R_1 to about R_2 , wherein:

- 25 (1) R_1 has a value ranging from about 1/64 inch to about 1/4 inch,
- (2) R_2 has a value ranging from about 1/64 inch to about 1/4 inch, and
- 30 (3) a value of a ratio R_2/R_1 ranges from about 1.0 to about 1.4; and an aspect ratio of less than about 2.0.

The catalyst may be employed in any hydrogenation process. Preferably, the catalyst is for producing a plug-flowing substantially packed bed of hydroprocessing catalyst during hydroprocessing by contacting a
35 substantially packed bed of hydroprocessing catalyst with an upflowing hydrocarbon feed stream. More particularly, when the catalytic particulates are disposed in a

-4-

hydrocarbon reaction zone, a substantially packed bed of hydroprocessing catalyst is produced; and when a hydrocarbon feed stream flows upwardly through the substantially packed bed of hydroprocessing catalyst, plug-flowing of the substantially packed bed of hydroprocessing catalyst commences when a volume of the catalytic particulates is withdrawn from a bottom of the hydrocarbon reaction zone. As used herein "catalyst" includes other particles which interact with a feed stream, such as sorbents, or other fluid contact bodies. The catalyst is disposed in a reaction zone and a hydrocarbon feed stream is flowed upwardly through the catalyst for hydroprocessing the hydrocarbon feed stream.

The catalytic particulates have a size distribution such that a maximum of about 2.0% by weight of said catalytic particulates have a diameter less than R_1 . The catalytic particulates also have a size distribution such that a maximum of about 0.4% by weight of the catalytic particulates have a diameter less than R_3 , wherein R_3 is less than R_1 and the value of the ratio R_1/R_3 is about 1.4. The catalytic particulates have a maximum attrition of about 1.0% by weight of the catalytic particulates through a diameter having a value of R_1 ; and the catalytic particulates have a maximum attrition of about 0.4% by weight of the catalytic particulates through a diameter having a value of R_3 , wherein R_3 is less than R_1 and the value of the ratio R_1/R_3 is about 1.4.

In one embodiment of the catalyst, the catalyst includes a plurality of catalytic particulates having a mean diameter ranging from about 6 Tyler mesh to about 8 Tyler mesh; and a size distribution such that at least about 97% by weight of the catalytic particulates have a diameter ranging from R_1 to R_2 , wherein:

- (1) R_1 has a value of about 0.093 inch;
- (2) R_2 has a value of about 0.131 inch; and include an aspect ratio of about 1.0; and wherein: the catalytic particulates have a maximum fines

-5-

content of up to about 1.0% by weight through 8 Tyler mesh and up to about 0.2% by weight through 10 Tyler mesh.

In another embodiment of the catalyst, the catalyst comprises a plurality of catalytic particulates having a mean diameter ranging from about 10 Tyler mesh to about 12 Tyler mesh; and a size distribution such that at least about 90% by weight of the catalytic particulates have a diameter ranging from R_1 to R_2 , wherein:

- (1) R_1 has a value of about 0.065 inch;
- (2) R_2 has a value of about 0.078 inch; and include an aspect ratio of less than about 2.0; and wherein: the catalytic particulates have a size distribution such that a maximum of about 2.0% by weight of the catalytic particulates have a diameter less than R_1 and a maximum of about 0.4% by weight of the catalytic particulates have a diameter less than R_2 , wherein R_2 is less than R_1 and the value of the ratio R_1/R_2 is about 1.4.

In yet another embodiment of the catalyst, the catalyst for hydroprocessing a hydrocarbon feed stream that is upflowing through a hydroconversion reaction zone having a substantially packed bed of the catalyst comprises a plurality of catalytic particulates having a mean diameter ranging from about 6 Tyler mesh to about 8 Tyler mesh; and a size distribution such that at least about 90% by weight of the catalytic particulates have a diameter ranging from R_1 to R_2 , wherein:

- (1) R_1 has a value of about 0.093 inch;
- (2) R_2 has a value of about 0.131 inch; and include an aspect ratio of less than about 2.0; and wherein: the catalytic particulates have a size distribution such that a maximum of about 2.0% by weight of the catalytic particulates have a diameter less than R_1 and a maximum of about 0.4% by weight of the catalytic

-6-

particulates have a diameter less than R_3 , wherein R_3 is less than R_1 and the value of the ratio R_1/R_3 is about 1.4.

In another aspect of the invention, the present invention also accomplishes its desired objects by broadly providing a method for producing an essentially downwardly plug-flowing substantially packed bed of hydroprocessing catalyst within a hydroconversion reaction zone comprising the steps of:

- 10 (a) forming a plurality of annular mixture zones under a hydroconversion reaction zone having a substantially packed bed of the hydroprocessing catalyst as described above such that each of the annular mixture zones contains a
15 hydrocarbon feed stream having a liquid component and a hydrogen-containing gas component and wherein the annular mixture zones are concentric with respect to each other and are coaxial with respect to the
20 hydroconversion reaction zone;
- (b) introducing the hydrocarbon feed stream from each of the annular mixture zones of step (a) into the substantially packed bed of hydroprocessing catalyst to commence upflowing
25 of the hydrocarbon feed stream from each of the annular mixture zones through the substantially packed bed of the catalyst;
- (c) withdrawing a volume of particulate catalyst from the hydroconversion reaction zone to
30 produce an essentially downwardly plug-flowing substantially packed bed of hydroprocessing catalyst within the hydroconversion reaction zone .

The method may further comprise injecting a quenching matter (e.g. a liquid quench) into the substantially packed bed of hydroprocessing catalyst

-7-

through a first conduit zone having a first conduit diameter; flowing the quenching matter from the first conduit zone into a second conduit zone having a second conduit zone diameter that is larger than the first
5 conduit diameter; flowing the quenching matter from the second conduit zone into a third conduit zone having a third conduit diameter that is smaller than the second conduit zone diameter; and injecting the quenching matter from the third conduit zone into the catalyst disposed in
10 the hydroconversion reaction zone which is having the hydrocarbon feed stream therethrough.

The substantially packed bed of hydroprocessing catalyst is disposed in the reactor zone within the reactor volume such that the substantially packed bed of
15 hydroprocessing catalyst maximally occupies the reactor volume. The substantially packed bed of hydroprocessing catalyst occupies at least about 50% by volume of the reactor volume; preferably at least about 60% by volume; and more preferably at least about 65% or 70% by volume
20 of the reactor volume.

From the foregoing summary it will be apparent that several significant factors contribute directly to the present invention accomplishing its desired objects, and to the efficient use of a given process reactor vessel to
25 assure non-ebullating, plug-like flow of a body of catalyst particles therethrough while being contacted by a counter-flowing hydrocarbon fluid stream of gas and liquid at maximum space-velocity. Among such significant factors are: (i) the size, volume and density
30 characteristics of such catalyst particles at preselectable flow velocities and pressures of the hydrocarbon fluid stream; (ii) control of catalyst bed ebullation and/or levitation during hydrocarbon fluid and hydrogen flows; (iii) laminar flow of the catalyst
35 particles during movement into and out of the catalyst moving bed for replacement (or regeneration or rejuvenation) without bed ebullation or levitation; (iv)

-8-

concentric annular feed of alternate rings of the gas and liquid components of the hydrocarbon feed uniformly into the full moving catalyst bed, which is capable of recovering promptly from upset or pressure changes in the reactor vessel to restore such alternate rings of gas and liquid over process runs of extended length (e.g. several thousand hours); and (v) redistribution of the gas components along the axial length of the moving bed.

10 Brief Description Of The Drawings

Fig. 1 is a partial cross-sectional view illustrating a catalytic bed with a plurality of superimposed layers with respect to each other before commencement of a plug-flow;

15 Fig. 2 is a partial cross-sectional view illustrating a catalytic bed which is moving downwardly in a plug-flow fashion;

Fig. 3 is a bottom plan view of the concentric and radial catalyst bed support means for a truncated conical or pyramidal screen;

20 Fig. 3A is a partial cross-sectional view of the reactor and a partial perspective view of another embodiment of the catalytic support means;

Fig. 4 is a partial cross-sectional view of the reactor and the catalytic support means of Fig. 3A which includes a plurality of annular mixture zones under the substantially packed bed of hydroprocessing catalyst with each annular mixture zone containing a liquid hydrocarbon component and a hydrogen-containing gas component and wherein the annular mixture zones are concentric with respect to each other and are coaxial with respect to the

30

-9-

imperforate center plate and supporting a plurality of segmented plates;

Fig. 6 is another cross-sectional view of the reactor and support means as similarly illustrated in Fig 5 with a bed of inert pellets having a liquid hydrocarbon component and a hydrogen-containing gas component flowing around the inert pellets for entering the annular mixture zones;

Fig. 7 is a horizontal cross-sectional series of the hydroprocessing vessel or reactor illustrating in top planar form the quench system(s) or assemblies for distributing a quench matter (i.e. a liquid quench and/or a gas quench) into a catalytic bed at a desired level therein;

Fig. 8 is a partial vertical sectional view taken in direction of the arrows and along the plane of line 8-8 in Fig. 7;

Fig. 8A is a partial sectional view disclosing a nozzle mounted on a quench conduit lateral; and

Fig. 9 is a partial vertical sectional view taken in direction of the arrows and along the plane of line 9-9 in Fig. 7.

Detailed Description of the Invention

Including Preferred Embodiments of the Invention

Referring in detail now to the drawings, and initially more particularly to Fig. 1, a hydroprocessing system is shown embodying the method of the present invention to increase substantially both the continued catalytic activity of a volume or bed of catalyst 10 and the efficient use of a single reactor vessel of a given reactor volume, such as reactor vessel 11. Vessel 11, as indicated by the thickness of its cylindrical side wall 12 and domed closure heads, or ends, 13 and 14, is designed to react a hydrogen containing gas mixed with a liquid hydrocarbon stream at a pressure of up to about

-10-

300 atmospheres (about 4500 lbs per square inch) and up to about 650° C. (about 1200° F.). Such reaction gas and a feed stream of hydrocarbon liquids are preferably premixed and introduced as a single stream through bottom head 13 by line 16.

To assure maximum catalytic benefit during the hydroprocessing of the hydrocarbon feed stream and the hydrogen-containing gas, it is essential that vessel 11 contain as much catalyst as possible within the design volume of vessel 11. Accordingly as indicated, support means 17 for catalyst bed 10 is placed as low as possible in vessel 11 while assuring full and adequate dispersion of the hydrogen phase within the liquid hydrocarbon stream. At the same time, the upper limit of bed 10 is near the top of domed head 14, while providing an adequate space 21 for disengaging any entrained catalyst from the resulting products withdrawn through center pipe 18. To insure that catalyst is not entrained into product fluids exiting through center pipe 18, a screen 15 may be installed in space 21 above a bed surface 20 defining the top of the catalyst bed 10. Fresh catalyst is then added to bed surface 20 through pipe 19 extending through screen 15. Desirably, the upper level or top of the catalyst bed 10, designated as the bed surface 20, is preferably controlled on a continuous basis by gamma ray absorption measurement made possible by a gamma ray source and gamma ray detector (not shown in the drawings) positioned in close proximity to the bed surface 20 of catalyst bed 10. Such a gamma ray source may be in the form of radioactive isotopes, such as Cesium 137, disposed inside the reactor in a specially designed well. Alternatively the source can be an electrically controllable source, such as a thermal neutron activated gamma ray generator. Detectors may be in the form of an ionization tube, Geiger-Mueller tube or a scintillation detector. Suitable sources and detectors are manufactured by Ronan Engineering Co., Texas Nuclear and

other vendors. By detecting the level of surface 20, it is possible, in accordance with the invention, to insure that the catalyst inventory is maintained at the optimum level and that the reactor is never overfilled.

5 Overfilling the reactor increases the chance that catalyst particles will be crushed in the isolation valves in the transfer lines when they are closed, at the end of each transfer. Bed level control is also needed to confirm that ebullation of the bed is minimized and
10 that undesirable excursions from the design flow rate for hydrogen and hydrocarbon feed flowing upwardly through bed 10 are avoided for the selected catalyst. To this end, the size, shape, and density of catalyst particles supplied to the bed are selected in accordance with the
15 designed maximum rate of flow of the feed streams to prevent such ebullation. Such control assures that bed 10 progressively moves down through vessel 11 in layers as by a plug flow. A "plug flow" of the catalyst bed 10 is illustrated in Figs. 1 and 2 and may be best described
20 as when a lowermost volumetric layer A is removed, the next volumetric layer B flows downwardly to replace the lowermost volumetric layer B and assumes a new position as a lowermost volumetric layer B. The removed lowermost volumetric layer A is replaced with an upper volumetric
25 layer J. The procedure is again repeated (as best shown by the dotted line representations in Fig. 2) by removing the lowermost volumetric layer B and causing the next volumetric layer C to flow downwardly in a plug-like fashion to replace the lowermost volumetric layer B and
30 assume a new position as a lowermost volumetric layer C.

-12-

For example, in a preferred embodiment of the present invention wherein metals (e.g. vanadium) are being removed from a hydrocarbon feed stream, the catalyst bed 10 is plug-flowing if a catalytic sample (e.g. 15 catalytic particulates) from withdrawn catalyst is analyzed and it is found through elemental metal analysis that the catalytic sample has a uniform high metal load, preferably at least about 1.5 times more than the average metal load of the catalyst bed 10, and more preferably at least about 2.0 times more than the average metal load of the catalyst bed 10. Those possessing the ordinary skill in the art can determine the average load of the catalyst bed 10 from the total amount of metals removed from the hydrocarbon feed stream, the weight of the catalytic bed 10, etc.

It is to be understood that whenever the specification or the claims states or mentions any type of catalyst movement or catalyst bed 10 movement (e.g. "removing", "moving", "supplying", "replacing", "delivering", "flow", "flowing", "transfer", "transferring", "addition", "adding", "admixing", etc.) for any type or mixture of catalyst without stating or mentioning the basis, the basis for such type of catalyst or catalyst bed movement may be on any type of basis, such as "intermittent basis", "periodic basis", "continuous basis", "semi-continuous basis", etc. Thus, by way of example only, removal of lowermost volumetric catalytic layers and addition of upper volumetric catalytic layers may be on a "periodic basis", "a continuous basis", or even "a one time basis", all without affecting the spirit and scope of the present invention(s). It is to be also understood that the "removal" or "withdrawal" of catalyst and the "addition" or "replacement" of catalyst are mutually exclusive of each other and may be performed simultaneously or at different times without affecting the spirit and scope and of the present invention(s). Preferably the

-13-

"addition" or "replacement" of catalyst is performed after the "removal" or "withdrawal" of catalyst and after the catalyst bed 10 has moved downwardly into a non-moving state or non-moving posture.

5 To further assure that plug flow continues throughout the full length of the bed, and particularly at the bottom portion, bed support means 17 is particularly characterized by the truncated polygonal or conical configuration of support means 17.

10 As shown in the preferred embodiment of Figs. 3-6, support 17 includes a series of annular polygons, approaching the form of annular rings, formed by a plurality of segment plates 27 (see Fig. 3) between radial ribs or spokes 26 extending from imperforate center plate 25 to sidewall 12 of vessel 11. As shown in Figs. 3 and 5, spokes 26 may be any suitable geometric shape, such as rod-like (see Fig. 5) or substantially flat plates (see Fig. 3), which divide the circumference of the vessel into many segments (eight in this case) and similarly support the ends of outer octagonal ring 23 of support means 17 formed by annular or circumferential plates 27. In each case, radial ribs or spokes 26, and annular segment plates 27 form a plurality of concentric rings, or annular polygons which support conical, or

25

-14-

pair or radial spokes 26. Thus, both phases flow upwardly through alternate concentric annular passages under screen 28. The preferential separation of gas from liquid in each ring includes an annular cap segment of gas overlying an adjacent lower annular segment filled with liquid. Hence, both fluids have equal, and angularly adjacent, access to the bed through screen 28. The plurality of alternate annular rings of hydrogen gas and hydrocarbon liquid assure even and equal feed of both phases across the full cross-sectional area of screen 28 into bed 10. Among other factors, we have particularly found that this configuration insures even and equal distribution across the full cross-sectional area of the catalyst bed. Such equal distribution across the full diameter of the bed 10, permits a quiescent flow section to form directly above center plate 25 which truncates conical bed support means 17. This decreases substantially potential local ebullation or eddy currents from being induced in the catalyst bed at the point of catalyst withdrawal through inlet 30 of inverted J-tube 29 to assure localized laminar flow of catalyst and liquid from within bed 10.

Uniform feed of the mixture of the hydrocarbon feed stream and hydrogen is particularly facilitated to the inlet side of plates 27 of support means 17 through plenum or inlet chamber 33 enclosed between support 17 and circular plate member 31, which extends across the full cross-sectional area of vessel 11. The circular plate member 31 defines a grid-like structure for supporting a permeable screen 6 having one or more openings, as best shown in Figs. 4, 5 and 6. As further best shown in Figs. 4, 5 and 6, the permeable screen 6

-15-

feed streams. Plate 31 includes a multiplicity of similar large diameter tubes 32 forming openings through plate 31. Each tube is several inches in diameter and extends axially to a similar depth, say on the order of 4 to 6 inches, below plate 31. Tubes 32 provide equal access to the mixture of hydrogen and hydrocarbon feed stream into plenum chamber 33. Even distribution of the incoming feed stream into bottom header 35 from feed line 16 may also be assisted by deflector plate 34 (see Figs. 1 and 2) to assure that oversized bubbles of hydrogen that may be contained in the feed stream will be equally distributed across the full cross-sectional area of plate 31 and equally distributed to each of tubes 32 for flow into plenum chamber 33. The length of tubes 32 may be selected to form a suitable gas head under plate 31 to suppress surges in the feed streams entering header 35.

As noted above, the vertical, transverse width or axial length of plates 27 which set off each individual annular and radial segment, provide equal access to both hydrogen and liquid feed into catalyst bed 10, and stepped under screen 28 so that they effectively form rings of gas and hydrocarbon feed alternately across the full diameter at the inlet side of catalyst bed 10. In this way, no single area of the inlet to catalyst bed 10 becomes a segregated or preferential, flow path for either gas or the liquid. Further, if pressure surges result in full wetting of screen 28 by the liquid phase, recovery of gas flow is assisted by the areal breadth of

-16-

the annular or circumferential plates 27 are secured to and are supported by the radial ribs or spokes 26, each of which has a vertical or transverse width that is essentially equal to the vertical or transverse width of the annular or circumferential plates 27. The radial ribs or spokes 26 also function as a means for reducing a size of hydrogen-containing gas bubbles, especially over-size hydrogen-containing gas bubbles from the hydrogen-containing gas component HG. Those skilled in the art will readily recognize that the number of radial ribs or spokes 26 employed will depend on a number of factors, such as the anticipated number of over-size hydrogen-containing gas bubbles in the upwardly flowing hydrocarbon feed stream, the weight of the catalyst bed 10, etc. The interconnected plates 27 and radial ribs or spokes 26 form a web or web-like structure defining a plurality of annular mixture zones, generally illustrated as MZ in Figs. 3-6. The annular mixture zones MZ are essentially continuous or are generally endless annular mixture zones MZ, and may contain or be subdivided into any reasonable desired number of mixture zones (or sub-mixture zones), such as MZ₁, MZ₂, MZ₃, MZ₄, MZ₅, and MZ₆ in Figs. 4 and 5. Each of the individual mixture zones MZ₁, MZ₂, MZ₃, MZ₄, MZ₅, and MZ₆ is for all practical purposes an annularly continuous or endless mixture zone of uniform thickness, excepting a periodic interruption by radially ribs 26, which are relatively narrow vis-a-vis the spaced distance between any pair of contiguous ribs 26-26. As evident in Figs. 3-6, concentric with mixture zone MZ₁ and as a partial bottom to same is imperforate center plate 25, which is preferably spaced from and off of the plate 31 and the screen 6 such that inert pellets 4 may be supported by the screen 6 and the plate 31 immediately underneath the imperforate center

-17-

and coupled plates 27,s and the perimeter of the
imperforate center plate 25.

The plurality of annular mixture zones MZ (or the
annularly continuous or endless mixture zones MZ₂s, MZ₃s,
5 MZ₄s, MZ₅s, and MZ₆s) under the catalyst bed 10 are
concentric with respect to each other and are coaxial
with respect to the reactor vessel 11 and the catalyst
bed 10. The plates 27 may be radially spaced from each
other at any suitable distance (preferably of uniform
10 distance) to assist in accomplishing the desired objects
of the present invention; however, preferably the plates
27 are radially spaced from each other at a generally
uniform thickness or distance that ranges from about 1
inch to about 4 feet, more preferably from about 6 inches
15 to about 3 feet, most preferably from about 1 foot to
about 2 feet. The radially spaced relationship between
and among the plates 27 generally defines a uniform
thickness for each of the mixture zones (i.e. MZ₂s, MZ₃s,
etc.). It is to be understood that while the plurality
20 of annular mixture zones MZ is represented in Figs. 3-6
as being a plurality of non-circular geometric-shaped
zones (e.g. octagonal in Fig. 3), the spirit and scope of
the present invention includes that the plurality mixture
zones MZ may comprise any geometric-shaped zones
25 including not only polygonal-shaped zones, but also a
plurality of concentric circular mixture zones.

-18-

or intercoupled plates 27_{1s}. The eight (8) plates 27_{1s} and the eight (8) plates 27_{2s} each form an annulate boundary for the essentially circular band of hydrocarbon feed stream in mixture zone MZ₂. Because the spacing or distance between plates 27_{1s} and 27_{2s} is generally circumferentially uniform, the thickness or size of the essentially circular band of hydrocarbon feed stream in mixture zone MZ₂ is essentially uniform transversely and/or equal in transverse or horizontal cross section. Similarly, mixture zone MZ₆ is defined by the eight (8) interengaged or intercoupled plates 27_{3s} and the eight (8) interengaged or intercoupled plates 27_{4s}, the combination of which form annulate boundaries for the essentially circular band of hydrocarbon feed stream in mixture zone MZ₆. As was previously similarly indicated for plates 27_{1s} and 27_{2s}, because the spacing or distance between plates 27_{3s} and 27_{4s} is generally circumferentially uniform, the thickness or size of the circular band of hydrocarbon feed stream in mixture zone MZ₆ is essentially uniform transversely and/or equal in transverse or horizontal cross section. Plates 27₂, 27₃, 27₄, and 27₅ similarly functionally interengage and intercouple to define annulate boundaries for mixture zones MZ₃, MZ₄, and MZ₅. As indicated and as best shown in Fig. 3, ribs 26 extend radially from imperforate center plate 25 and planarly represent visually pie-shaped segments. Between any pair of contiguous ribs 26-26, the lengths of the respective plates 27 increase from

vertical dimensions or the widths of the plates 27 (i.e. the structural extensions of the plates 27 that are generally parallel to the longitudinal axis of the reactor vessel 11 and/or the catalyst bed 10 therein) are generally equal. All plates 27 are preferably spaced such that the hydrocarbon feed stream flows parallel to the longitudinal axis of the catalyst bed 10 before contacting and entering the same. Both the upper edges and lower edges of plates 27_{1s}, 27_{2s}, 27_{3s}, 27_{4s}, 27_{5s}, and 27_{6s} are all at a different level or height. The mixture zones MZ differ from a plurality of tubes, conduits, or pipe-like passages for introducing an essentially complete or essentially total integral cylindrical hydrocarbon feed stream into the catalytic bed 10. As best shown in Figs. 4 and 5, the upper and lower edges of plates 27_{1s} are at a different level or height than the upper and lower edges of plates 27_{2s} which are at a different level or height than the upper and lower edges of plates 27_{3s}. Similarly, the upper and lower edges of plates 27_{3s} are at a different level or height than the upper and lower edges of plates 27_{4s} which are at a different level or height than the upper and lower edges of plates 27_{5s}. The upper and lower edges of the latter are at a different level or height than the upper and lower edges of plates 27_{6s}.

After the LH-HG mixture enters and flows through the screen 6 into the plenum chamber 33, the flowing LH-HG mixture enters into each of the generally continuous

mixture zones MZ_{1s}, MZ_{2s}, etc. for dividing or

-20-

hydrocarbon feed stream (i.e. hydrocarbon liquid feed and/or hydrogen gas) in and through the space by which it is being defined. In a preferred embodiment of the present invention and as best shown in Fig. 6, before the
5 flowing LH-HG mixture enters into each of the generally continuous annular mixture zones MZ_1s , MZ_2s , MZ_3s , etc. the LH-HG mixture flows around the plurality of inert pellets 4 in zig-zag fashions for reducing the possibility of eddy currents and for keeping bubbles of
10 hydrogen gas diffused within the liquid hydrocarbon and preventing agglomeration of same into larger size bubbles. The hydrocarbon feed stream entering into mixture zone MZ_1 is designated LH-HG₁. The plurality of LH-HG mixtures (i.e. LH-HG₁, LH-HG₂, etc.) pass through
15 the screen 28 and respectively enter into the catalyst bed 10 from each of the mixture zones (i.e. MZ_1s , MZ_2s , MZ_3s , etc.) at a flow rate such as not to ebullate, levitate or expand the catalyst bed 10 upwardly and/or towards the screen 15 and the domed head 14 by more than
20 10% by length beyond substantially the full axial length of the bed catalyst 10 in a packed bed state, such as the

-21-

stream into plenum chamber 33 from and through line 16,
are all to be controlled in an amount and to an extent
sufficient to maintain expansion or levitation of the
catalyst bed 10 to less than 10% by length over or beyond
5 substantially the full axial length of the bed 10 in a
packed bed state. More preferably, the expansion of the
substantially packed bed of catalyst is limited to less
than 5%, most preferably less than 2% or even less than
1%, by length over or beyond substantially the full axial
10 length of the bed 10 in a packed bed state. Ideally the
expansion of the substantially packed bed of catalyst is
limited to essentially 0% by length.

The flow rate of the hydrocarbon feed stream through
line 16 is to be at a rate not substantially greater than
15 the optimum rate of flow. The optimum rate of process
fluid flow through the substantially packed bed of
catalyst will vary from process unit to process unit
based on several factors including oil and hydrogen feed
characteristics, catalyst specifications, process
20 objectives, etc. Based on catalyst particles having
substantially the same and/or uniform size, shape and
density, the flow rate of the hydrocarbon feed stream
preferably ranges from about 0.01 ft/sec to about 10.00
ft/sec and more preferably from about 0.01 ft/sec to
25 about 1.00 ft/sec. Similarly and/or likewise and further
based on the catalyst particles having substantially the
same and/or uniform size, shape, and density, the flow

-22-

hydroprocessing process. The specific flow rates however would be at any suitable rate controlled in an amount and to an extent sufficient to limit expansion of the substantially packed bed of catalyst to less than 10% by length over or beyond a substantially packed bed of hydroprocessing catalyst in a packed bed state.

In a preferred embodiment of the invention and for such a flow rate for the hydrocarbon feed stream and for such a flow rate for the continuous annular LH-HG mixtures, the catalyst particles preferably have the substantially same and/or uniform size, shape and density in order to obtain over the desired demetallization and/or desulfurization of the liquid hydrocarbon component LH in the hydrocarbon feed stream (i.e. LH-HC mixture) into produced hydrogen upgraded product fluids that are being withdrawn from the reactor vessel 11 through the center pipe 18. At the above indicated flow rates for the hydrocarbon feed stream flowing through line 16, and for the flow rates for the generally continuous annular LH-HG mixtures (i.e. LH-HG₁, LH-HG₂, etc.), the produced upgraded product fluids are being preferably withdrawn through the center pipe 18 from the reactor vessel 11 at a rate ranging from about 0.01 ft/sec to about 10.00 ft/sec and more preferably from about 0.01 ft/sec to about 1.00 ft/sec. The withdrawal rate(s) of the produced upgraded product fluids is not to be greater than the optimum rate of flow and will also vary from process unit to process unit based on several factors including oil and hydrogen feed characteristics, catalyst specifications, process objectives, etc. The specific withdrawal rate(s) would be any suitable withdrawal rate, controlled in an amount and to an extent sufficient to prevent and/or limit expansion of the

-26-

the secondary quench medium furnishing assembly 132.

Longitudinal extremities or opposed ends of the primary hollow quench medium receiving member 138 or quench conduit header 142 have a pair of guided type header supports (or primary supports), generally illustrated as 182-182, respectively secured thereto and to the support means 134 (more specifically to a skirt member identified as 180 below). The header (or primary) supports 182-182 operate to couple the primary hollow quench medium receiving member 138 (or quench conduit header 142) to the support means 132. The header (or primary) supports 182-182 may be manufactured from any suitable material, preferably from any thermal expansive material that would be compatible with metallurgical requirements to support the primary hollow quench medium receiving member 138 or quench conduit header 142 in a depending relationship with respect to the support means 132 while allowing for some freedom of movement due to thermal expansion.

The primary quench medium furnishing assembly 130 also includes a quenching medium inlet member 140 that passes through the cylindrical side wall 12 of the reactor vessel 11 and secures and/or couples to the header inlet conduit 146a for transmitting or conducting a quenching medium or matter into the header inlet conduit 146a, which in turn transmits or conducts the same for subsequent flow into the primary hollow quench medium receiving member 138 (or the quench conduit header 142). As previously indicated, the quenching medium or matter originates from a quenching source that has been previously obtained and disposed outside of the reactor vessel 11. The quenching medium inlet member 140 is

-23-

packed bed state.

The arrangement in inlet distributor 31 for uniformly distributing hydrogen gas and liquid hydrocarbon feed as shown in Fig. 4 may be modified by
5 lengthening or shortening tubes 32, forming uniformly distributed cylindrical passageways into plenum chamber 33. A particular advantage of using tubes 32, as compared to merely perforations or holes of adequate diameter, lies in the formation of a gas pocket under
10 plate 31 in the areas around the individual tubes 32. We have found that this is desirable because such a gas pocket trapped beneath tray or plate 31 provides pressure surge dampening, which may result from flow changes of the mixture of hydrogen and liquid being supplied to the
15 reactor vessel. However, the length of the tubes 32 is maintained as short as reasonably possible to so function. Again, this is because of the desirability of utilizing as little as possible of all processing space available in vessel 11 for anything but contacting the
20 feed streams with conversion catalyst. A particular advantage to using tubes 32, as compared to a combination of tubes and perforations, is that the designed flow distribution pattern is maintained over a wider range of flow rates. With tubes and perforations, gas normally
25 flows up the perforations and liquid flows up the tubes. However, gas will find new flow paths through the tubes if the gas flow increases or the perforations become plugged, resulting in undesigned and potentially undesirable flow patterns.

30 Referring in detail now to Figs. 7-9 for an embodiment of the quench system 39 for not only further assisting in maintenance of plug-like flow of catalyst bed 10 throughout its axial length, but to also assist in: (i) reducing hydrogen-containing gas traffic (i.e.
35 hydrogen-containing gas component velocity) in the upper reaction zones of the catalyst bed 10 to the extent that

-24-

packed (catalytic) bed conditions; (ii) transferring reactor interstage cooling or quench load responsibility from an all process quench gas medium to a quench medium selected from the group consisting of quench gas, quench liquid, and mixtures thereof, or in some instances to a quench medium consisting entirely of process quench liquid; and (iii) controlling the quench gas portion of any combined liquid/gas quench medium to maintain hydrogen-containing gas balance based on hydroprocessing process chemical requirements, and not necessarily the complete cooling and/or quenching requirements, and (iv) switching primary control of reactor interstage cooling and/or quenching to a quench liquid matter or quench liquid stream that is backed up automatically by a quench gas matter or quench gas stream in the event that flow of the quench liquid matter or quench liquid stream is interrupted for some reason. The quench system 39 in this preferred embodiment of the present invention may be employed with and/or within any type of hydroprocessing process including but not limited to fixed bed hydroprocessing, ebullated or expanded bed hydroprocessing, etc.

The quench system 39 for the embodiment of the invention depicted in Figs. 7-9 comprises a primary quench medium furnishing assembly, generally illustrated as 130; and a secondary quench medium furnishing assembly, generally illustrated as 132 and secured to and/or coupled to and communicating with the primary quench medium furnishing assembly 130 for receiving a quench medium or matter (i.e. a liquid quench and/or a gas quench) and for distributing the same into the catalyst bed 10 in accordance with a procedure to be further explained in detail hereafter. A support means,

-25-

assemblies 130 and 132 for maintaining the primary and secondary quench medium furnishing assemblies 130 and 132 in a suspended relationship within and with respect to the catalyst bed 10 and for keeping the two assemblies
5 130 and 132 in a generally stationary posture with respect to the reactor vessel 11.

The primary quench medium furnishing assembly 130 preferably comprises a primary hollow quench medium receiving member 138, which is preferably a quench
10 conduit header 142, for receiving a quench or quenching medium or matter that has been or is being transported thereto from a source for quenching external to the reactor vessel 11.

The primary hollow quench medium receiving member
15 138 or quench conduit header 142 is formed with one or more or a plurality of generally hollow transverse members or transverse header conduits 150 that extend generally normally therefrom and communicate with the primary hollow quench medium receiving member 138 or
20 quench conduit header 142. The plurality of transverse header conduits 150 possess a diameter (i.e. an internal diameter) that is less than or smaller than the diameter of the quench conduit header 142. As best shown in Fig. 8, the primary hollow quench medium receiving member
25 138 (or quench conduit header 142) is also formed with a header inlet conduit (or secondary inlet conduit) 146a which communicates with the primary hollow quench medium receiving member 138 (or quench conduit header 142) for receiving and passing a quench medium or matter into the
30 latter. The header inlet conduit 146a has a diameter (i.e. an internal diameter) that is less than or smaller than a diameter (i.e. an internal diameter) of the quench conduit header 142. The diameter of the latter is larger than that of the quenching medium inlet conduit
35 146 in order to be able to obtain, or otherwise receive,

-27-

146 is coupled to the header inlet conduit 146a by a coupling clamp (or a means for coupling), generally illustrated as 158, which functions as a connecting and disconnect vehicle or member to permit the quenching medium inlet conduit 146 to be easily connected or secured to the header inlet conduit 146a and to facilitate the disconnection of the two inlet conduits 146 and 146a for any desired reason, such as for the cleaning and/or unplugging of inlet conduit 146 and/or 146a, etc. The coupling clamp 158 may be any suitable coupling means or assembly that is capable of coupling, connecting and disconnecting any pair of members or conduit members to accomplish the purpose of the quench system 39 for this preferred embodiment of the invention.

A suitable coupling clamp 158 is one sold under the registered trademark GRAYLOC[®] by ABB VETCO GRAY of Houston, Texas. The quenching medium inlet conduit 146 feeds the primary hollow quench medium receiving member 138 (i.e. the quench conduit header 142 and its associated header inlet conduit 146a) at a situs that is generally coaxial with respect to a longitudinal axis of the reactor vessel 11 and/or the catalyst bed 10.

The secondary quench medium furnishing assembly 132 comprises one or more or a plurality of quench conduit laterals 154 which have a diameter (i.e. an internal diameter) that approximate the diameter of the transverse header conduits 150. Each of the quench conduit laterals 154 is secured and/or coupled to a respective transverse header conduit 150 via the coupling clamp 158

which as previously indicated may be

-28-

Fig. 9), secured thereto and to the support means 134 (more specifically to a skirt member identified hereinafter as 180). The lateral supports 184 operate to couple a quench conduit lateral 154 to the support means 134. The lateral supports 184 may be manufactured from any suitable material, preferably from any thermal expansive material that would be compatible with metallurgical requirements to support the secondary quench medium furnish assembly 132 or the quench conduit laterals 154 in a depending relationship with respect to the support means 132 while allowing for some freedom of movement due to thermal expansion.

Each of the quench conduit laterals 154 is formed with one or more orifices or apertures 160 that communicate(s) with a nozzle assembly, generally illustrated as 164, to permit a quenching medium or matter to pass from the quench conduit lateral(s) 154 into the nozzle assembly 164 for subsequent injection and distribution into the catalyst bed 10. The one or more orifices or apertures 160 are designed to uniformly distribute quenching medium (i.e. quenching liquid and/or quenching gas) into the catalyst bed 10.

Each nozzle assembly 164 is connected to the quench conduit lateral(s) 154 (and/or to the quench conduit header 142) such as to project upwardly towards the dome head 14 of the reactor vessel 11 and generally parallel to the longitudinal axis of the reactor vessel 11.

However, the spirit and scope of the present invention includes securing at least one or more of the nozzle assemblies 164 to the quench conduit lateral(s) 154 (and/or to the quench conduit header 142) such as to project downwardly or towards a bottom of a

either concurrent or countercurrent with the flow of a hydrocarbon feed passing through a bed of catalyst.

The support means 134 may be any suitable support means for supporting the quench medium furnishing assemblies 130 and 132 in a desired position within the catalyst bed 10 of the reactor vessel 11, but preferably comprises a skirt member 180, and a support coupling member 188 fastened to the skirt member 180. The skirt support member 180 is preferably configured or designed to be cylindrically ring-like and the support coupling member 188 connects to an outer circumferential surface thereof and to the insides of the cylindrical side wall 12. As was previously indicated, the pair of header (or primary) supports 182-182 also connect to the skirt support member 180 (more specifically to an inside circumferential surface of the skirt support member 180) for coupling and/or interconnecting the primary hollow quench medium receiving member 138 or quench conduit header 142 to the skirt support member 180. As was also previously indicated, the lateral supports 184 also connect to the skirt support member 180 (more specifically to an inside circumferential surface of the skirt support member 180) for coupling and/or interconnecting the secondary quench medium furnishing assembly 132, more specifically the quench conduit lateral(s) 154, to the skirt support member 180. The support coupling member 188 supports the present preferred embodiment of the quench system 39 within and away from the reactor vessel 11 (i.e. within and away

-30-

5 catalyst at a rate of flow such that expansion of the substantially packed bed of hydroprocessing catalyst is limited to less than 10% by length beyond a substantially full axial length of the substantially packed bed of hydroprocessing catalyst in a packed bed state. A volume of the hydroprocessing catalyst is withdrawn from the reactor zone to commence essentially plug-flowing downwardly of the substantially packed bed of hydroprocessing catalyst within the reactor zone; and

10 hydroprocessing replacement catalyst is added to the essentially plug-flowing downwardly, substantially packed bed of hydroprocessing catalyst at a rate to substantially replace the volume of the withdrawn hydroprocessing catalyst. The procedure may be repeated

15 as many times as desired, even continuously repeated during continual hydroprocessing.

Another method is provided for hydroprocessing a hydrocarbon feed stream that is upflowing through a hydroconversion reaction zone having a substantially

20 packed bed of catalyst which comprises forming a plurality of annular mixture zones under a hydroconversion reaction zone having a substantially packed bed of hydroprocessing catalyst such that each of the annular mixture zones contains a hydrocarbon feed

25 stream having a liquid component and a hydrogen-containing gas component and wherein the annular mixture zones are concentric with respect to each other and are coaxial with respect to the hydroconversion reaction

-31-

contacting the catalyst bed in a hydroconversion reaction zone with an upflowing hydrocarbon feed stream having a liquid component and a hydrogen-containing gas component, comprising the steps of:

5 (a) disposing a plurality of catalytic particulates in a hydroconversion reaction zone to form a catalyst bed having at least one upper reaction zone and at least one lower reaction zone;

10 (b) upflowing into the catalyst bed of step (a) a hydrocarbon feed stream having a liquid component and a hydrogen-containing gas component, until steady-state conditions have been essentially reached and the catalytic particulates in the upper reaction zone have an upper activity level and the catalytic particulates in
15 the lower reaction zone have a lower activity level differing from the upper activity level;

(c) withdrawing a volume of particulate catalyst from the lower reaction zone in the hydroconversion reaction zone, wherein the withdrawn volume of
20 particulate catalyst includes a high-activity less dense catalytic particulates and a low-activity more dense catalytic particulates;

(d) separating the high-activity less dense catalytic particulates from the low-activity more dense
25 catalytic particulates;

(e) admixing the high-activity less dense catalytic particulates with fresh catalytic particulates to produce a catalytic mixture;

(f) introducing the catalytic mixture of step (e)

-32-

hydroprocessing catalyst in a substantially packed bed of catalyst downwardly moving in a hydroconversion reaction zone during hydroprocessing (especially at equilibrium or steady-state conditions) by contacting the

5 hydroprocessing catalyst in the hydroconversion reaction zone with an upflowing hydrocarbon feed stream having a liquid component and a hydrogen-containing gas component, comprising the steps of:

10 (a) withdrawing a volume of particulate catalyst from a hydroconversion reaction zone having a substantially packed bed of hydroprocessing catalyst which is essentially plug-flowing downwardly in the hydroconversion reaction zone and wherein the withdrawn volume of particulate catalyst includes a high-activity less dense catalytic particulates and a low-activity more

15 dense catalytic particulates;

(b) separating the high-activity less dense catalytic particulates from the low-activity more dense catalytic particulates;

20 (c) admixing the high-activity less dense catalytic particulates with fresh catalytic particulates to produce a catalytic mixture; and

(d) introducing the catalytic mixture of step (c) into the hydroconversion reaction zone of step (a) for

25 increasing upgrading and/or demetallization capabilities of said hydroprocessing catalyst in said substantially packed bed of hydroprocessing catalyst which is essentially plug-flowing downwardly in the hydroconversion reaction zone of step (a).

30 The present invention also accomplishes its desired objects by broadly providing a method for reducing the quantity of hydroprocessing catalyst required for upgrading a hydrocarbon feed stream (or stated alternatively for extending a life of hydroprocessing

35 catalyst in a hydroconversion reaction zone) during hydroprocessing by contacting the hydroprocessing

-33-

upflowing hydrocarbon feed stream having a liquid component and a hydrogen-containing gas component. The reduction of the quantity of hydroprocessing catalyst required in accordance with the present invention provides or allows for upgrading a hydrocarbon feed stream to essentially the same degree as and/or when compared to the quantity of hydroprocessing catalyst required for upgrading the hydrocarbon feed stream in a once through hydroprocessing catalyst replacement mode. The method broadly comprises the steps of:

(a) withdrawing a volume of particulate catalyst from a hydroconversion reaction zone having a substantially packed bed of hydroprocessing catalyst having an initially packed bed volume and which is essentially plug-flowing downwardly in the hydroconversion reaction zone and wherein the withdrawn volume of particulate catalyst includes a high-activity less dense catalytic particulates and a low-activity more dense catalytic particulates;

(b) separating the high-activity less dense catalytic particulates from the low-activity more dense catalytic particulates;

(c) admixing the high-activity less dense catalytic particulates with fresh catalytic particulates to produce a catalytic mixture having a mixture volume that is less than the withdrawn volume of particulate catalyst; and

(d) introducing subsequently the catalytic mixture into the hydroconversion reaction zone such that the substantially packed bed, which is essentially plug-flowing downwardly in the hydroconversion reaction zone,

-34-

catalyst comprising the steps of:

- 5 (a) forming a plurality of annular mixture zones under a hydroconversion reaction zone having a substantially packed bed of hydroprocessing catalyst such that each of the annular mixture zones contains a hydrocarbon feed stream having a liquid component and a hydrogen-containing gas component and wherein the annular mixture zones are concentric with respect to each other and are coaxial with respect to the hydroconversion reaction zone;
- 10 (b) introducing the hydrocarbon feed stream from each of the annular mixture zones into the substantially packed bed of hydroprocessing catalyst to commence upflowing of the hydrocarbon feed stream from each of the annular mixture zones through the substantially packed bed of the catalyst and to produce a volume of particulate catalyst in the hydroconversion reaction zone having a high-activity less dense catalytic particulates and a low-activity more dense catalytic particulates;
- 20 (c) withdrawing the volume of particulate catalyst from the hydroconversion reaction zone to commence essentially plug-flowing downwardly the substantially packed bed of hydroprocessing catalyst within the hydroconversion reaction zone;
- 25 (d) separating the high-activity less dense catalytic particulates from the low-activity more dense catalytic particulates;
- 30 (e) admixing the high-activity less dense catalytic particulates with fresh catalytic particulates to produce a catalytic mixture; and
- (f) introducing the catalytic mixture into the hydroconversion reaction zone.

35 A hydroconversion system and/or a hydroconversion reaction zone of a present preferred embodiment of the present invention contains a catalyst which is described in detail below under the following subtitle "The

-35-

Catalyst", and may also be operated as a fixed bed (i.e. a catalyst bed which does not expand), a moving bed, an ebullated bed, an expanded bed or a fluidized bed configuration.

5

THE CATALYST

In a preferred embodiment of the invention, the catalyst which is charged to the reactor vessel 11 preferably satisfies the following four main criteria: (i) the catalyst has the appropriate catalytic activity and life for the particular application (e.g. demetallation, hydrodesulfurization, etc.); (ii) the catalyst has physical properties which minimize its random motion in the reactor vessel 11; (iii) the catalyst has physical properties which minimize catalyst loss both in the catalyst transfer steps and in the reactor vessel 11; and (iv) the catalyst is sufficiently uniform in size and shape and density to prevent classification by size in normal operation.

The catalyst in the present invention preferably has the appropriate catalytic activity and life for the specific application (e.g. demetallation, hydrodesulfurization, etc.). For example, if the catalyst is to be used for demetallation, it should have sufficient HDM activity and metals loading capacity (i.e. life) to meet the target demetallation without the use of uneconomic amounts of catalyst. The metals loading capacity of the catalyst is preferably greater than about 0.10 grams of metal per cubic centimeter of catalyst bulk volume and is more preferably greater than about 0.20 grams metal per cubic centimeter of catalyst bulk volume. The catalyst properties which most affect catalytic activity and metals loading capability are: pore structure (pore volume and pore size distribution); base material (e.g. alumina versus silica); catalytic metals (amount, distribution, and type (nickel, molybdenum, cobalt, etc.)); surface area; and particle size and distribution.

-36-

The catalyst in the present invention also preferably has physical properties which minimize catalyst lifting into random motion in the upflow type reactor vessel 11. Since one of the benefits of the present invention is the countercurrent contacting that is achieved between the reactants and catalyst, it is preferred to maintain plug flow of the catalyst downwards through the entire length of the reactor vessel 11. The catalyst properties which are critical to minimizing or preventing catalyst expansion are: catalyst particle density (highest particle density possible is preferred while still meeting catalytic activity and metals loading requirements); particle size (largest size practical is preferred); skeletal density (higher skeletal density is preferred to reduce skeletal buoyancy); and size uniformity. One of the salient features of the present invention is that the catalyst will not expand into random motion in the reactor vessel 11, but will still move rather easily during flow transportation. Under actual process conditions within the reactor, significantly smaller catalysts could rise to the top while significantly larger catalysts could migrate to the bottom. This intervenes with optimal plug flow movement of catalyst. For this reason, size specifications for the catalysts of the present invention are narrower than those for fully packed or fixed bed and ebullated bed catalysts.

-37-

strength (maximum crush strength is required without producing a catalyst which is very brittle and might suffer from excessive attrition); catalyst size and shape (spherical catalyst are preferred since they move more easily and have no rough or sharp edges to break off); and fines content (minimum fines is an absolute requirement to avoid adverse effects in the reactor vessel 11 and downstream equipment).

The catalyst is sufficiently uniform in size and shape and density to prevent classification by size in normal operation. Generally, narrow specifications are required for the catalyst to prevent classification by size. Specific catalyst size is selected so that it is near the point of being expanded into random motion, but not to the point of expansion into random motion per se or ebullation.

All of the four main criteria for the selection of the catalyst of the present invention are important and are not independent or mutually exclusive of each other. The four main criteria must be balanced against each other to optimize the catalyst for the specific application. For example, to minimize catalyst expansion into random motion we would prefer a large and very dense catalyst. This is contrary to the properties we might want for a residuum demetallation application where we need a small particle with low density diameters. These competing needs must be balanced to ensure minimum

-38-

The catalyst of the present invention unexpectedly produces a plug-flowing substantially packed bed (i.e. catalyst bed 10) of hydroprocessing catalyst during hydroprocessing by contacting a substantially packed bed of hydroprocessing catalyst with an hydrocarbon feed stream (i.e. a liquid component and a hydrogen-containing gas component) that is upflowing at a rate controlled in an amount and to an extent sufficient to limit expansion of the substantially packed bed of hydroprocessing catalyst to less than 10% by length beyond a substantially full axial length of the substantially packed bed of hydroprocessing catalyst in a packed bed state. More preferably, the expansion of the substantially packed bed of hydroprocessing catalyst is limited to less than 5%, most preferably less than 2% or even less than 1% , by length beyond a substantially full axial length of the substantially packed bed of hydroprocessing catalyst in a packed bed state. The rate of flow of the hydrocarbon feed stream may be any suitable rate controlled in an amount and to an extent sufficient to limit the expansion of the substantially packed bed of hydroprocessing catalyst, preferably the rate of flow is at a rate ranging from about 0.01 ft/sec. to about 10.00 ft/sec.

The catalyst of the present invention more specifically unexpectedly produces a plug-flowing substantially packed bed of hydroprocessing catalyst when

-39-

the present invention maximally and optimally occupies a volume within the reactor vessel 11 that is larger or greater than a volume of a bed of catalyst in an ebullating reactor vessel that has substantially the same entire internal and/or inside available volume as the reactor vessel 11 and wherein the volume of the bed of catalyst in the ebullating reactor vessel is in a "slumped" (or packed) catalyst bed condition or state. Typically, a bed of catalyst in an ebullating reactor vessel in a "slumped" catalyst bed condition occupies approximately up to less than about 50% by volume (maximum) of the entire internal and/or inside available volume of the ebullating reactor vessel. Thus, the substantially packed bed of hydroprocessing catalyst maximally and optimally occupies at least about 50% by volume, preferably from about 80% by volume to about 98% by volume of the entire internal and/or inside available volume of the reactor vessel 11. Most preferably, the substantially packed bed of hydroprocessing catalyst of the present invention maximally and optimally occupies from about 85% by volume to about 95% by volume of the entire internal and/or inside available volume of the reactor vessel 11.

The catalyst of the present invention furthermore specifically unexpectedly produces the plug-flowing substantially packed bed of hydroprocessing catalyst when

-40-

transferred to commence plug-flow, it is transferred or withdrawn preferably laminarly in the liquid component of the hydrocarbon feed stream and is removed from above and in proximity to an impervious zone (i.e. imperforate center plate 25) of the bed support means 17 and substantially out of the flow path of the LH-HG mixtures (i.e. LH-HG₂, LH-HG₃, etc.) emanating out of the mixture zones MZ (i.e. MZ_{2S}, MZ_{3S}, etc.). The particular volume (or amount) of catalyst that is withdrawn at any desired time from the bottom of the substantially packed bed of hydroprocessing catalyst may be any suitable volume or amount which accomplishes the desired objectives of the present invention. Preferably, such as by way of example only, the particular volume or amount of catalyst that is withdrawn at any desired time is a volume or amount ranging from about 0.10% by weight to about 25.00% by weight of the substantially packed bed (i.e. catalyst bed 10). The rate of withdrawal of a particular volume (or amount) of catalyst may also be any suitable volume or amount which accomplishes the desired objectives of the present invention, such as a rate of withdrawal where the flow rate of the catalyst (e.g. the catalyst in the hydrocarbon feed stream) ranges from about 0.1 ft/sec. to about 20 ft/sec., more preferably from about 0.1 ft/sec. to about 10 ft/sec., and at a catalyst concentration ranging from about 0.10 lbs catalyst/lb. catalyst slurry (i.e. weight of hydroprocessing catalyst plus weight of hydrocarbon feed stream) to about 0.80 lbs catalyst/lb. catalyst slurry, more preferably from about 0.15 lbs catalyst/lb. catalyst slurry to about 0.60 lbs catalyst/lb. catalyst slurry. As previously indicated, the withdrawn catalyst may be conveniently replaced by introducing a volume of fresh catalyst through the top of the reactor vessel 11 onto the catalyst bed 10. The replacement or catalyst addition rate may be any suitable replacement or catalyst addition rate which will accomplish the desired objects of the present invention,

-41-

such as a flow replacement rate of the replacement catalyst (i.e. the replacement catalyst in the hydrocarbon refined stream (e.g. gas oil)) ranging from about 0.1 ft/sec. to about 20 ft/sec., more preferably from about 0.1 ft/sec. to about 10 ft/sec., and at a catalyst replacement concentration ranging from about 0.10 lbs. replacement catalyst/lb. catalyst slurry (i.e. weight of replacement catalyst plus the hydrocarbon refined stream (e.g. gas oil) as the slurring medium) to about 0.80 lbs replacement catalyst/lb. catalyst slurry, more preferably from about 0.15 lbs catalyst/lb. catalyst slurry to about 0.60 lbs catalyst/lb. catalyst slurry.

In a preferred embodiment of the present invention, the catalyst of the present invention comprises an inorganic support which may include zeolites, inorganic oxides, such as silica, alumina, magnesia, titania and mixtures thereof, or any of the amorphous refractory inorganic oxides of Group II, III or IV elements, or compositions of the inorganic oxides. The inorganic support more preferably comprises a porous carrier material, such as alumina, silica, silica-alumina, or crystalline aluminosilicate. Deposited on and/or in the inorganic support or porous carrier material is one or more metals or compounds of metals, such as oxides, where the metals are selected from the groups Ib, Vb, VIb, VIIb, and VIII of the Periodic System. Typical examples of these metals are iron, cobalt, nickel, tungsten, molybdenum, chromium, vanadium, copper, palladium, and platinum as well as combinations thereof. Preference is given to molybdenum, tungsten, nickel, and cobalt, and combinations thereof. Suitable examples of catalyst of the preferred type comprise nickel-tungsten, nickel-molybdenum, cobalt-molybdenum or nickel-cobalt-molybdenum deposited on and/or in a porous inorganic oxide selected from the group consisting of silica, alumina, magnesia, titania, zirconia, thoria, boria or hafnia or compositions of the inorganic oxides, such as silica-

-42-

alumina, silica-magnesia, alumina-magnesia and the like.

The catalyst of the present invention may further comprise additives which alter the activity and/or metals loading characteristics of the catalyst, such as but not limited to phosphorus and clays (including pillared clays). Such additives may be present in any suitable quantities, depending on the particular application for the hydroconversion process including the applied catalyst. Typically, such additives would comprise essentially from about zero (0)% by weight to about 10.0% by weight, calculated on the weight of the total catalyst (i.e. inorganic oxide support plus metal oxides).

Although the metal components (i.e. cobalt, molybdenum, etc.) may be present in any suitable amount, the catalyst of the present invention preferably comprises from about 0.1 to about 60 percent by weight of metal component(s) calculated on the weight of the total catalyst (i.e. inorganic oxide support plus metal oxides) or and more preferably of from about 0.2 to about 40 percent by weight of the total catalyst, and most preferably from about 0.5 to about 30 percent by weight

-43-

the particular hydroprocessing application for the catalyst and/or on the processing objectives.

5 The groups in the Periodic System referred to above are from the Periodic Table of the Elements as published in Lange's Handbook of Chemistry (Twelfth Edition) edited by John A. Dean and copyrighted 1979 by McGraw-Hill, Inc., or as published in The Condensed Chemical Dictionary (Tenth Edition) revised by Gessner G. Hawley and copyrighted 1981 by Litton Educational Publishing
10 Inc.

In a more preferred embodiment for the catalyst, the oxidic hydrotreating catalyst or metal oxide component carried by or borne by the inorganic support or porous carrier material is molybdenum oxide (MoO_3) or a
15 combination of MoO_3 and nickel oxide (NiO) where the MoO_3 is present in the greater amount. The porous inorganic support is more preferably alumina. The Mo is present on the catalyst inorganic support (alumina) in an amount ranging from about 0.5 to about 50 percent by weight,
20 preferably from about 0.5 to about 30 percent by weight, most preferably from about 1.0 to about 20 percent by weight, based on the combined weight of the inorganic

-44-

The catalyst has a surface area (such as measured by the B.E.T. method) sufficient to achieve the hydroprocessing objectives of the particular application. Surface area is typically from about 50 sq. meters per gram to about 300 sq. meters per gram, more typically from about 75 sq. meters per gram to about 150 sq. meters per gram.

The catalyst mean crush strength should be a minimum of about 5 lbs. Crush strength may be determined on a statistical sample of catalytic particulates. For example, a fixed number (say 30 catalyst particles) are obtained from a statistical lot comprising a plurality of catalyst particles that are to be employed in the hydrogenation process of the present invention. Each catalyst particle is subsequently disposed between two horizontal and parallel steel plates. A force is then applied to the top steel plate until the disposed catalyst particle breaks. The force applied to break the catalyst particle is the crush strength. The test is repeated for the remaining catalyst particles, and a mean crush strength is obtained. Preferably further, no more than about 35% by wt. of the catalyst particles or catalytic particulates have a mean crush strength of less than about 5 lbs.; more preferably, no more than about 15% by wt. of the catalyst particles or catalytic particulates have a mean crush strength of less than about 5 lbs; and most preferably, no more than about 0% by wt.

The catalyst of the present invention comprises a plurality of catalytic particulates having a uniform size, which is preferably spherical with a mean diameter having a value ranging from about 35 Tyler mesh to about 3 Tyler mesh, more preferably ranging from about 20 Tyler mesh to about 4 Tyler mesh, and most preferably from about 14 Tyler mesh to about 5 Tyler mesh. The Tyler mesh designations referred to herein are from a table entitled "Tyler Standard Screen Scale Sieves" in the 1981

-45-

Edition of Handbook 53, published by CE Tyler Combustion Engineering, Inc., 50 Washington St., South Norwalk, Conn. 06856.

5 Likewise, the preferred catalyst particle has a uniformly smooth and rounded surface. Preferred shapes include, for example, spheres, spheroids, egg-shaped particles and the like. More preferably, the catalyst of the present process is a rounded particle including a plurality of catalytic particulates having a size
10 distribution such that at least about 90% by weight of said catalytic particulates have an aspect ratio of less than about 2.0, more preferably equal to or less than about 1.5, and most preferably about 1.0. As used herein, "aspect ratio" is a geometric term defined by the
15 value of the maximum projection of a catalyst particle divided by the value of the width of the catalyst particle. The "maximum projection" is the maximum possible catalyst particle projection. This is sometimes called the maximum caliper dimension and is the largest
20 dimension in the maximum cross-section of the catalyst particle. The "width" of a catalyst particle is the catalyst particle projection perpendicular to the maximum projection and is the largest dimension of the catalyst particle perpendicular to the maximum projection.

25 The catalyst should have a particle size distribution such that the catalyst bed 10 expands under the conditions within the reactor vess 1 11 to less than 10% by length (more preferably less than 5% and most

-46-

at least about 97% by weight, of the catalytic particulates in the catalyst bed 10 have a diameter ranging from R_1 to R_2 , wherein: (i) R_1 has a value ranging from about 1/64 inch (i.e. the approximate opening size of a 35 mesh Tyler screen) to about 1/4 inch (i.e. the approximate opening size of a 3 mesh Tyler screen); (ii) R_2 also has a value ranging from about 1/64 inch (i.e. the approximate opening size of a 35 mesh Tyler screen) to about 1/4 inch (i.e. the approximate opening size of a 3 mesh Tyler screen); and (iii) the ratio R_2/R_1 has a value greater than or equal to about 1 and less than or equal to about 1.4 (or about the square root of 2.0). More preferably, the catalytic particulates in the catalyst bed 10 have a diameter ranging from R_1 to R_2 wherein R_1 and R_2 each has a value ranging from about 2/64 inch (i.e. the approximate opening size of a 20 mesh Tyler screen) to about 12/64 inch (i.e. the approximate opening size of a 4 mesh Tyler screen), most preferably from about 3/64 inch (i.e. the approximate opening size of a 14 mesh Tyler screen) to about 9/64 inch (i.e. the approximate opening size of a 5 mesh Tyler screen), and wherein the ratio R_2/R_1 has a value ranging from about 1.00 to about 1.4 (or about the square root of 2.0).

25 The catalyst employed in the hydrogenation process of the present invention also broadly comprises a size

-47-

ratio R_1/R_3 is about 1.4 (or about the square root of 2.0). The catalyst particles or catalytic particulates of the catalyst preferably have a maximum attrition of about 1.0% by weight (more preferably a maximum of about 0.5% by weight and most preferably a maximum of about 0.25% by weight or less) of the catalyst particles or catalytic particulates through a diameter (i.e., a Tyler screen opening) having a value of R_1 , and a further maximum attrition of about 0.4% by weight (more preferably a maximum attrition of about 0.2% by weight and most preferably a maximum attrition of about 0.1% by weight or less) of the catalyst particles or catalytic particulates through a diameter (i.e., again a Tyler screen opening) having a value of R_3 wherein R_3 again (as stated above) is less than R_1 and the value of the ratio of R_1/R_3 is about 1.4 (or about the square root of 2.0). [Note that the attrition procedure is specified in ASTM D 4058-87. However, in the standard method, the fines are removed through a 850μ (~20 mesh) screen. In the present method, the screen is an opening equal to the minimum catalyst size desired for the particular application, as more specifically defined by the value of R_1 and R_3 .] Thus, by way of example only, for a catalyst with a specified size range of about 10 to about 12 Tyler mesh, one would specify up to about 2.0% by wt. fines (more preferably up to about 1.0% by wt.) MAX through 12 Tyler mesh and up to about 0.4% by wt. (more preferably up to about 0.2% by wt.) MAX through 14 Tyler mesh. Similarly, for a catalyst with a specified size range of about 6 to about 8 Tyler mesh, one would specify up to about 2.0% by wt. fines (more preferably up to about 1.0% by wt. fines) MAX through 8 Tyler mesh and up to about 0.4% by wt. fines (more preferably up about 0.2% by wt. fines) MAX through 10 Tyler mesh. For the catalyst with the specified size range of about 10 to about 12 mesh, one would specify an attrition of up to about 1.0% by wt. (more preferably up to about 0.5% by

-48-

wt., most preferably up to about 0.25% by wt.) MAX through 12 Tyler mesh and up to about 0.4% by wt., (more preferably up to about 0.2% by wt., most preferably up to about 0.1% by wt.) MAX through 14 Tyler mesh. Similarly
5 further, for catalyst with the specified size range of about 6 to about 8 Tyler mesh, one would specify an attrition of up to about 1.0% by wt. (more preferably up to about 0.5% by wt., most preferably up to about 0.25% by wt.) MAX through 8 Tyler mesh and up to about 0.4% by
10 wt. (more preferably up to about 0.2% by wt., and most preferably up to about 0.1% by wt.) MAX through 10 Tyler mesh.

The specific particle density of the catalyst particles is determined by the requirements of the
15 hydroconversion process. For the present invention it is preferred that the catalyst particles have a uniform density. By "uniform density" is meant that the density of at least about 70% by weight, preferably at least about 80% by weight, and more preferably at least about
20 90% by weight, of the individual catalyst particles do not vary by more than about 10% from the mean density of all catalyst particles; and more preferably the individual catalyst particles do not vary by more than about 5% from the mean density of all of the particles.

25 In a preferred embodiment of the present invention the catalyst (i.e. fresh catalyst) has a particle density ranging from about 0.6 g/cc to about 1.5 g/cc, more preferably from about 0.7 g/cc to about 1.2 g/cc, most preferably from about 0.8 g/cc to about 1.1 g/cc. After
30 the catalyst has at least been partially spent, the particle density would range from about .6 g/cc to about 3.0 g/cc, more preferably from about .7 g/cc to about 3.0 g/cc and most preferably from about 0.8 g/cc to about 3.0

-49-

While the catalyst of the present invention may be any catalyst as defined above, we have discovered that the more preferred catalyst for optimally accomplishing the objectives of the present invention comprises in combination the following properties: (i) a porous inorganic oxide support; (ii) one or more catalytic metals and/or additional catalytic additives deposited in and/or on the porous inorganic oxide support; (iii) a crush strength at least about 5 pounds force; (iv) a uniform size ranging from about 6 to about 8 Tyler mesh sizes; (v) a fines content up to about 1.0 percent by weight through 8 Tyler mesh and up to about 0.2 percent by weight through 10 Tyler mesh; (vi) an attrition up to about 0.5 percent by weight through 8 Tyler mesh and up to of about 0.2 percent by weight through 10 Tyler mesh; (vii) a generally uniform spherical shape; and (viii) a uniform density ranging from about 0.7 g/cc to about 3.0 g/cc. We have discovered unexpectedly that the more preferred catalyst having or containing the immediate foregoing combination of properties, unexpectedly produces in an optimal fashion the plug-flowing substantially packed bed (i.e. catalytic bed 11) of hydroprocessing catalyst which is simultaneously expanding to less than 10 percent by length (more preferably less than 1% by length) beyond a substantially full axial length of the substantially packed bed of hydroprocessing catalyst in a packed bed state while (and simultaneously with) the substantially packed bed of hydroprocessing catalyst maximally and optimally occupying from about 50 percent by volume to about 98 percent by volume (i.e. the entire internal and/or inside available volume or reactor volume) of the reactor vessel 11.

The particular type of porous base material or inorganic oxide support, the particular type of catalytic metal, the pore structure, the catalyst surface area and catalyst size, would all depend on the intended specific

-50-

application (e.g. demetallation, desulfurization, etc.)
of the catalyst. Generally, the more preferred catalyst
comprises a porous inorganic oxide support selected from
the group consisting alumina, silica, and mixtures
5 thereof, and has a surface area ranging from about 75
square meters per gram to about 150 square meters per
gram. The preferred catalyst comprises catalytic
metal(s), present as oxide(s) deposited in and/or on the
porous inorganic support. Oxide(s) of the catalytic
10 metal(s), or the metallic oxide component of the
preferred catalyst, is selected from the group consisting
of molybdenum oxide, cobalt oxide, nickel oxide, tungsten
oxide, and mixtures thereof, and comprises from about 0.5
to about 50 percent by weight, more preferably from about
15 0.5 to about 30 percent by weight, of the total catalyst
(i.e. inorganic oxide support plus metal oxide(s)). The
more preferred catalyst further comprises a general
uniform spherical shape having a mean diameter ranging
from about 20 Tyler mesh to about 4 Tyler mesh. While a
20 spherical shaped catalyst is the more preferred catalyst,
an extrudate may be employed if it is very strong, say
having a crush strength over 5 lbs. of force. The
absolute size of the catalyst may vary from application
to application, but the more preferred catalyst has the
25 narrow size distribution as previously stated above.

From the foregoing discussion it will be clear to
the skilled practitioner that, though the catalyst
particles of the present process have a uniform size,
shape, and density, the chemical and metallurgical nature
30 of the catalyst may change, depending on processing
objectives and process conditions selected. For
example, a catalyst selected for a demetallation
application with minimum hydrocracking desired, could be
quite different in nature from a catalyst selected if
35 maximum hydrodesulfurization and hydrocracking are the

-51-

above, is disposed in any hydroconversion reaction zone. A hydrocarbon feed stream is passed through the catalyst, preferably passed through such as upflow through the catalyst, in order to hydroprocess the hydrocarbon feed stream. More preferably, the catalyst is employed with the various embodiments of the present invention.

EXAMPLE

A plurality of catalytic particulates were charged into a reaction zone contained within a reactor, such as reactor vessel 11. The plurality of catalytic particulates formed a catalyst bed (such as catalyst bed 10 in Figs. 1 and 2). The catalyst bed was supported in the reactor by a truncated conical bed support similar to the support that is generally illustrated as 17 in Figs. 1 and 2. An inlet distributor, such as circular plate member 31 in Figs. 1 and 2 with the multiplicity of tubes 32, extended across a full cross-sectional area of the reactor underneath the truncated conical bed support to form a plenum or inlet chamber between the inlet distributor and the truncated conical bed support. The truncated conical bed support for the catalyst bed included a series of annular polygons that included a plurality of segmented plates (such as segmented plates 27 in Figs. 4-6) connected to or formed with radial spoke members such as members 26 Figs. 3-6. The plurality of segmented plates, each having a thickness of about 10 inches and a width of about 1.5 inch, were secured to 8 radial spoke members. The inter engaged segmented plates and radial spoke members formed a web-like structure to produce essentially annularly continuous mixture zones for receiving a flow of hydrocarbon feed stream, and were overlaid with a screen having screen openings with a mean diameter that was smaller than the catalytic

-52-

The catalytic particulates comprised an alumina porous carrier material or alumina inorganic support. Deposited on and/or in the alumina porous carrier material was an oxidic hydrotreating catalyst component consisting of NiO and/or MoO₃. The Mo was present on and/or in the alumina porous carrier material in an amount of about 3% by wt., based on the combined weight of the alumina porous carrier material and the oxidic hydrotreating catalyst component(s). The Ni was present on and/or in the alumina porous carrier material in an amount of about 1% by wt., based on the combined weight of the alumina porous carrier material and the oxidic hydrotreating catalyst component(s). The surface area of the catalytic particulates was about 120 sq. meters per gram.

The plurality of catalytic particulates were generally spherical with a mean diameter having a value ranging from about 6 Tyler mesh to about 8 Tyler mesh. The mean crush strength of the catalytic particulates was about 5 lbs. force. The metals loading capacity of the catalyst or plurality of catalytic particulates was about 0.3 grams of metal per cubic centimeter of catalytic particulate bulk volume.

The catalytic particulates had a size distribution such that 98.5% by weight of the catalytic particulates in the catalyst bed had an aspect ratio of about 1.0 and a diameter ranging from R_1 to R_2 wherein: (i) R_1 had a value of about 0.093 inch (i.e. the approximate opening of an 8 mesh Tyler screen); (ii) R_2 had a value of about

-53-

a diameter less than R_3 , wherein R_3 was less than R_1 and the value of the ratio R_1/R_3 was about the square root of 2.0 or about 1.414.

5 The catalytic particulates of the catalyst had a maximum attrition of about 0.5% by weight of the catalytic particulates through a diameter (i.e. a Tyler screen opening) having the value of R_1 , and a further maximum attrition of about 0.2% by weight of the catalytic particulates through a diameter (i.e. a Tyler
10 screen opening) having the value of R_3 wherein R_3 again was less than R_1 and the value of the ratio of R_1/R_3 was about the square root of 2.0 or about 1.414. Stated alternatively, for the catalytic particulates with the specified size range or distribution of about 6 to about
15 8 Tyler mesh, the specified attrition for the catalytic particulates was up to about 0.5% by weight MAX through 8 Tyler mesh and up to about 0.2% by weight MAX through 10 Tyler mesh.

20 The catalytic particulates had a maximum fines content of up to about 1.0% by wt. through 8 Tyler mesh and up to about 0.2% by wt. through 10 Tyler mesh

pure hydrogen and was mixed with the heavy atmospheric residuum stream in a mixing ratio of 623 liters of hydrogen-containing gas at standard conditions per liter of heavy atmospheric residuum in order to form the hydrocarbon feed stream.

The hydrocarbon feed stream was passed through the inlet distributor and introduced into the plenum chamber of reactor at a flow rate ranging from about 0.1 ft/sec. to about 1.00 ft/sec. The hydroprocessing pressure and temperature within the reactor were about 2300 psig. and about 400°C respectively. From the plenum chamber of the reactor the hydrocarbon feed stream entered into the annular continuous mixture zones and was uniformly fed through the screen and into the catalyst bed such as not to induce local ebullation or eddy currents in the catalyst bed, especially in proximity to the conical bed support which was overlayed with the screen.

The catalyst bed in the reactor contained a plurality of axially spaced apart hydrogen gas redistribution (or hydrogen gas-quenching) assemblies (see Figs. 7 through 9 as illustrative of the hydrogen gas-quenching assemblies). As the hydrocarbon feed

-55-

upwardly through the catalyst bed, a gamma ray source in the catalyst bed in combination with a gamma ray detector on the reactor detected that the catalyst bed expanded less than 10% by length over or beyond substantially the full axial length of the catalyst bed in a packed bed state.

After the reactor was on stream for about 1 weeks, approximately 7.25 cubic meters (or about 3.3% by weight of the catalyst bed) of catalytic particulates were laminarly withdrawn in the hydrocarbon feed stream through a J-tube (such as J-tube 29 in Fig. 1) at a flow rate of about 3.6 ft/sec. The withdrawn catalyst in the hydrocarbon feed stream had a concentration of about 0.5 lbs. catalyst/lb. catalyst slurry (i.e. weight of withdrawn catalyst plus weight of hydrocarbon feed stream). When and/or as the volume of catalytic particulates were withdrawn or transferred from the bottom of the catalyst bed, the catalyst bed (i.e. a substantially packed bed of catalyst) began to plug-flow.

The withdrawn catalyst was replaced by introducing a comparable volume of fresh replacement catalyst through the top of the reactor. The fresh replacement catalyst was slurried in a hydrocarbon refined stream (e.g. gas oil) and was introduced into the reactor at a flow catalyst replacement rate of about 3.6 ft/sec., and at a catalyst replacement concentration of about 0.5 lbs. replacement catalyst/lb. catalyst slurry (i.e. weight of replacement catalyst plus the hydrocarbon refined stream (e.g. gas oil) as the slurring medium).

While the present invention has been described herein with reference to particular embodiments thereof, a latitude of modification, various changes and substitutions are intended in the foregoing disclosure, and it will be appreciated that in some instances some features of the invention will be employed without a corresponding use of other features without departing from the scope of the invention as set forth.

-56-

WE CLAIM:

1. A method for hydroprocessing a hydrocarbon feed stream that is upflowing through a hydroconversion reaction zone having a substantially packed bed of catalyst comprising the steps of:
 - (a) disposing catalyst in a reaction zone, said catalyst comprising a plurality of catalytic particulates having a mean diameter ranging from about 35 Tyler mesh to about 3 Tyler mesh; and a size distribution such that at least about 90% by weight of said catalytic particulates have a diameter ranging from R_1 to R_2 , wherein:
 - (1) R_1 has a value ranging from about 1/64 inch to about 1/4 inch,
 - (2) R_2 has a value ranging from about 1/64 inch to about 1/4 inch,
 - (3) a value of a ratio R_2/R_1 ranges from about 1.0 to about 1.4; an aspect ratio of less than about 2.0; and
 - (b) upflowing through said catalyst of step (a) a hydrocarbon feed stream for hydroprocessing the hydrocarbon feed stream.
2. The method of Claim 1 wherein said catalytic particulates have a size distribution such that a maximum of about 2.0% by weight of said catalytic particulates have a diameter less than R_1 .
3. The method of Claim 2 wherein said catalytic particulates have a size distribution such that a maximum of about 0.4% by weight of said catalytic particulates have a diameter less than R_3 , wherein R_3 is less than R_1 and the value of the ratio R_1/R_3 is about 1.4.

-57-

4. The method of Claim 1 wherein said catalytic particulates have a maximum attrition of about 1.0% by weight of said catalytic particulates through a diameter having a value of R_1 .

5

5. A method for hydroprocessing a hydrocarbon feed stream that is upflowing through a hydroconversion reaction zone having a substantially packed bed of catalyst comprising the steps of:

10

- (a) forming a plurality of annular mixture zones under a hydroconversion reaction zone having a substantially packed bed of hydroprocessing catalyst such that each of said annular mixture zones contains a hydrocarbon feed stream having a liquid component and a hydrogen-containing gas component and wherein said annular mixture zones are concentric with respect to each other and are coaxial with respect to said hydroconversion reaction zone, and wherein said hydroprocessing catalyst comprises a plurality of catalytic particulates having a mean diameter ranging from about 35 Tyler mesh to about 3 Tyler mesh; and a size distribution such that at least about 90% by weight of said catalytic particulates have an aspect ratio of less than about 2.0 and a diameter ranging from R_1 to R_2 , wherein:

15

20

25

30

- (1) R_1 has a value ranging from about 1/64 inch to about 1/4 inch,
(2) R_2 has a value ranging from about 1/64 inch to about 1/4 inch;
(3) a value of a ratio R_2/R_1 ranges from about 1.0 to about 1.4; and

35

- (b) introducing said hydrocarbon feed stream from each of said annular mixture zones of step (a) into said substantially packed bed of hydroprocessing catalyst to commence upflowing

-58-

of said hydrocarbon feed stream from each of said annular mixture zones through said substantially packed bed of the catalyst.

5 6. The method of Claim 5 wherein said step (b) introducing said hydrocarbon feed stream from each of said annular mixture zones of step (a) into said substantially packed bed of hydroprocessing catalyst comprises flowing upwardly said hydrocarbon feed stream from each of said annular mixture zones of step (a) into said substantially packed bed of hydroprocessing catalyst at a rate of flow such that said substantially packed bed of hydroprocessing catalyst expands to less than 10% by length beyond a substantially full axial length of said substantially packed bed of hydroprocessing catalyst in a packed bed state.

20 7. The method of Claim 5 additionally comprising withdrawing a volume of said hydroprocessing catalyst from said reactor zone to commence essentially plug-flowing downwardly of said substantially packed bed of hydroprocessing catalyst within said reactor zone; and adding hydroprocessing replacement catalyst to said essentially plug-flowing downwardly, substantially

25

-59-

having a mean diameter ranging from about 35 Tyler mesh to about 3 Tyler mesh; and a size distribution such that at least about 90% by weight of said catalytic particulates have a diameter ranging from R_1 to R_2 , wherein:

- (1) R_1 has a value ranging from about 1/64 inch to about 1/4 inch,
- (2) R_2 has a value ranging from about 1/64 inch to about 1/4 inch,
- (3) a value of a ratio R_2/R_1 ranges from about 1.0 to about 1.4; and

an aspect ratio less than about 2.0, and wherein: said catalytic particulates have a size distribution such that a maximum of about 2.0% by weight of said catalytic particulates have a diameter less than R_1 and maximum of about 0.4% by weight of said catalytic particulates have a diameter less than R_3 , wherein R_3 is less than R_1 and the value of the ratio R_1/R_3 is about 1.4; such that when said catalytic particulates are disposed in a hydrocarbon reaction zone to produce a substantially packed bed of hydroprocessing catalyst and a hydrocarbon feed stream flows upwardly through the substantially packed bed of hydroprocessing catalyst, plug-flowing of the substantially packed bed of hydroprocessing catalyst commences when a volume of said catalytic particulates is withdrawn from a bottom of the hydrocarbon reaction zone.

9. The catalyst of Claim 8 wherein said catalytic particulates have a maximum attrition of about 0.4% by weight of said catalytic particulates through a diameter having a value of R_3 , wherein R_3 is less than R_1 and the value of the ratio of R_1/R_3 is about 1.4.

-60-

10. The method of Claim 1 additionally comprising injecting a quenching matter into said catalyst.
- 5 11. The method of Claim 5 additionally comprising injecting a quenching matter into said catalyst.
- 10 12. The method of Claim 10 wherein said injecting comprises passing the quenching matter through a first conduit zone having a first conduit diameter; flowing the quenching matter from the first conduit zone into a second conduit zone having a second conduit zone diameter that is larger than the first conduit diameter; flowing the quenching matter from the second conduit zone into a third conduit zone having a third conduit diameter that is smaller than the second conduit zone diameter; and injecting the quenching matter from the third conduit zone into the catalyst disposed in the hydroconversion reaction zone which is having the hydrocarbon feed stream flowing therethrough.
- 15 20
- 25 13. The method of Claim 11 wherein said injecting comprises passing the quenching matter through a first conduit zone having a first conduit diameter; flowing the quenching matter from the first conduit zone into a second conduit zone having a second conduit zone diameter that is larger than the first conduit diameter; flowing the quenching matter from the second conduit zone into a third conduit zone

-61-

14. The method of Claim 5 wherein in order for increasing the activity level of catalytic particulates in a lower reaction zone of the hydroprocessing catalyst bed during hydroprocessing by contacting the catalyst bed in the hydroconversion reaction zone with the upflowing hydrocarbon feed stream having a liquid component and a hydrogen-containing gas component, said method additionally comprising the steps of:

- (c) disposing this plurality of catalytic particulates in the hydroconversion reaction zone to form the catalyst bed having at least one upper reaction zone and at least one lower reaction zone;
- (d) upflowing into the catalyst bed of step (a) the hydrocarbon feed stream having the liquid component and the hydrogen-containing gas component, until steady-state conditions have been essentially reached and the catalytic particulates in the upper reaction zone have an upper activity level and the catalytic particulates in the lower reaction zone have a lower activity level differing from the upper activity level;
- (e) withdrawing a volume of particulate catalyst from the lower reaction zone in the hydroconversion reaction zone, wherein the withdrawn volume of particulate catalyst includes a high-activity less dense catalytic particulates and a low-activity more dense catalytic particulates;
- (f) separating the high-activity less dense catalytic particulates from the low-activity more dense catalytic particulates;
- (g) admixing the high-activity less dense catalytic particulates with fresh catalytic particulates

-62-

to produce a catalytic mixture;

- (h) introducing the catalytic mixture of step (g) into said hydroconversion reaction zone of step (c); and

5

- (i) repeating steps (e) through (h) until steady-state conditions have been essentially reached and catalytic particulates in the lower reaction zone of the catalyst bed have an activity level that is greater than the lower activity level of step (d).

10

15

20

15. The method of Claim 5 wherein in order for increasing upgrading capabilities and/or demetallization of the hydroprocessing catalyst in the substantially packed bed of catalyst downwardly moving in the hydroconversion reaction zone during hydroprocessing (especially at equilibrium or steady-state conditions) by contacting the hydroprocessing catalyst in the hydroconversion reaction zone with the upflowing hydrocarbon f d

-63-

- (e) admixing the high-activity less dense catalytic particulates with fresh catalytic particulates to produce a catalytic mixture; and
- 5 (f) introducing the catalytic mixture of step (e) into the hydroconversion reaction zone of step (c) for increasing upgrading and/or demetallization capabilities of said hydroprocessing catalyst in said substantially packed bed of hydroprocessing catalyst which is
- 10 essentially plug-flowing downwardly in the hydroconversion reaction zone of step (c).

16. The method of Claim 5 wherein in order for reducing the quantity of the hydroprocessing catalyst
- 15 required for upgrading the hydrocarbon feed stream (or stated alternatively for extending the life of hydroprocessing catalyst in the hydroconversion reaction zone) during hydroprocessing by contacting the hydroprocessing catalyst in the hydroconversion
- 20 reaction zone with the upflowing feed stream having a liquid component and a hydrogen-containing gas component such that the reduction of the quantity of hydroprocessing catalyst required provides or allows for upgrading the hydrocarbon feed stream to
- 25 essentially the same degree as and/or when compared to the quantity of hydroprocessing catalyst required for upgrading the hydrocarbon feed stream in a one through hydroprocessing catalyst replacement mode, said method additionally comprising the steps of:

30

- (c) withdrawing a volume of particulate catalyst from the hydroconversion reaction zone having

-64-

catalyst includes a high-activity less dense catalytic particulates and a low-activity more dense catalytic particulates;

- 5 (d) separating the high-activity less dense catalytic particulates from the low-activity more dense catalytic particulates;
- (e) admixing the high-activity less dense catalytic particulates with fresh catalytic particulates to produce a catalytic mixture having a mixture
- 10 volume that is less than the withdrawn volume of particulate catalyst; and

- (f) introducing subsequently the catalytic mixture into the hydroconversion reaction zone such
- 15 that the substantially packed bed, which is essentially plug-flowing downwardly in the hydroconversion reaction zone, has a subsequent packed bed volume that is less than the initially packed bed volume.

20

17. The method of Claim 13 wherein in order for increasing the activity level of catalytic particulates in a lower reaction zone of the hydroprocessing catalyst bed during hydroprocessing
- 25 by contacting the catalyst bed in the hydroconversion reaction zone with the upflowing hydrocarbon feed stream having a liquid component and a hydrogen-containing gas component, said method additionally comprising the steps of:

30

- (c) disposing this plurality of catalytic particulates in the hydroconversion reaction zone to form the catalyst bed having at least one upper reaction zone and at least one lower
- 35 reaction zone;
- (d) upflowing into the catalyst bed of step (a) the hydrocarbon feed stream having the liquid

-65-

component and the hydrogen-containing gas component, until steady-state conditions have been essentially reached and the catalytic particulates in the upper reaction zone have an upper activity level and the catalytic particulates in the lower reaction zone have a lower activity level differing from the upper activity level;

- (e) withdrawing a volume of particulate catalyst from the lower reaction zone in the hydroconversion reaction zone, wherein the withdrawn volume of particulate catalyst includes a high-activity less dense catalytic particulates and a low-activity more dense catalytic particulates;
- (f) separating the high-activity less dense catalytic particulates from the low-activity more dense catalytic particulates;
- (g) admixing the high-activity less dense catalytic particulates with fresh catalytic particulates to produce a catalytic mixture;
- (h) introducing the catalytic mixture of step (g) into said hydroconversion reaction zone of step (c); and
- (i) repeating steps (e) through (h) until steady-

-66-

hydrocarbon feed stream having a liquid component and a hydrogen-containing gas component, said method additionally comprising the steps of:

- 5 (c) disposing this plurality of catalytic particulates in the hydroconversion reaction zone to form the catalyst bed having at least one upper reaction zone and at least one lower reaction zone;
- 10 (d) upflowing into the catalyst bed of step (a) the hydrocarbon feed stream having the liquid component and the hydrogen-containing gas component, until steady-state conditions have been essentially reached and the catalytic
15 particulates in the upper reaction zone have an upper activity level and the catalytic particulates in the lower reaction zone have a lower activity level differing from the upper activity level;
- 20 (e) withdrawing a volume of particulate catalyst from the lower reaction zone in the hydroconversion reaction zone, wherein the withdrawn volume of particulate catalyst includes a high-activity less dense catalytic
25 particulates and a low-activity more dense catalytic particulates;
- (f) separating the high-activity less dense catalytic particulates from the low-activity more dense catalytic particulates;
- 30 (g) admixing the high-activity less dense catalytic particulates with fresh catalytic particulates to produce a catalytic mixture;
- (h) introducing the catalytic mixture of step (g) into said hydroconversion reaction zone of step (c); and
- 35 (i) repeating steps (e) through (h) until steady-state conditions have been essentially reached and catalytic particulates in the lower

-67-

reaction zone of the catalyst bed have an activity level that is greater than the lower activity level of step (d).

- 5 19. The method of Claim 1 wherein in order for
increasing upgrading capabilities and/or
demetallization of the hydroprocessing catalyst in
the substantially packed bed of catalyst downwardly
moving in the hydroconversion reaction zone during
10 hydroprocessing (especially at equilibrium or
steady-state conditions) by contacting the
hydroprocessing catalyst in the hydroconversion
reaction zone with the upflowing hydrocarbon feed
stream having a liquid component and a hydrogen-
15 containing gas component, said method additionally
comprising the steps of:

- (c) withdrawing a volume of particulate catalyst
from the hydroconversion reaction zon having
20 the substantially packed bed of hydroprocessing
catalyst which is essentially plug-flowing
downwardly in the hydroconversion reaction zone
and wherein the withdrawn volume of particulate

-68-

packed bed of hydroprocessing catalyst which is essentially plug-flowing downwardly in the hydroconversion reaction zone of step (c).

- 5 20. The method of Claim 1 wherein in order for reducing the quantity of the hydroprocessing catalyst required for upgrading the hydrocarbon feed stream (or stated alternatively for extending the life of hydroprocessing catalyst in the hydroconversion
10 reaction zone) during hydroprocessing by contacting the hydroprocessing catalyst in the hydroconversion reaction zone with the upflowing feed stream having a liquid component and a hydrogen-containing gas component such that the reduction of the quantity of
15 hydroprocessing catalyst required provides or allows for upgrading the hydrocarbon feed stream to essentially the same degree as and/or when compared to the quantity of hydroprocessing catalyst required for upgrading the hydrocarbon feed stream in a once
20 through hydroprocessing catalyst replacement mode, said method additionally comprising the steps of:

- 25 (c) withdrawing a volume of particulate catalyst from the hydroconversion reaction zone having the substantially packed bed of hydroprocessing

-69-

to produce a catalytic mixture having a mixture volume that is less than the withdrawn volume of particulate catalyst; and

- 5 (f) introducing subsequently the catalytic mixture into the hydroconversion reaction zone such that the substantially packed bed, which is essentially plug-flowing downwardly in the hydroconversion reaction zone, has a subsequent packed bed volume that is less than the
- 10 initially packed bed volume.

21. A method for hydroprocessing a hydrocarbon feed stream that is upflowing through a hydroconversion reaction zone having a substantially packed bed of catalyst comprising the steps of:
- 15

- (a) forming a plurality of annular mixture zones under the hydroconversion reaction zone having a substantially packed bed of hydroprocessing catalyst such that each of said annular mixture zones contains a hydrocarbon feed stream having a liquid component and a hydrogen containing gas component and wherein said annular mixture zones are concentric with respect to each other and are coaxial with respect to said
- 20
- 25 hydroconversion reaction zone;

- (b) introducing said hydrocarbon feed stream from

-70-

- (c) injecting a quenching matter into said substantially packed bed of hydroprocessing catalyst;
- 5 (d) withdrawing a volume of particulate catalyst from said hydroconversion reaction zone to commence essentially plug-flowing downwardly said substantially packed bed of hydroprocessing catalyst within said
10 hydroconversion reaction zone; and
- (e) adding a volume of catalyst to the hydroconversion reaction zone of step (d) to replace the withdrawn volume of particulate
15 catalyst of step (d).

FIGURE 1

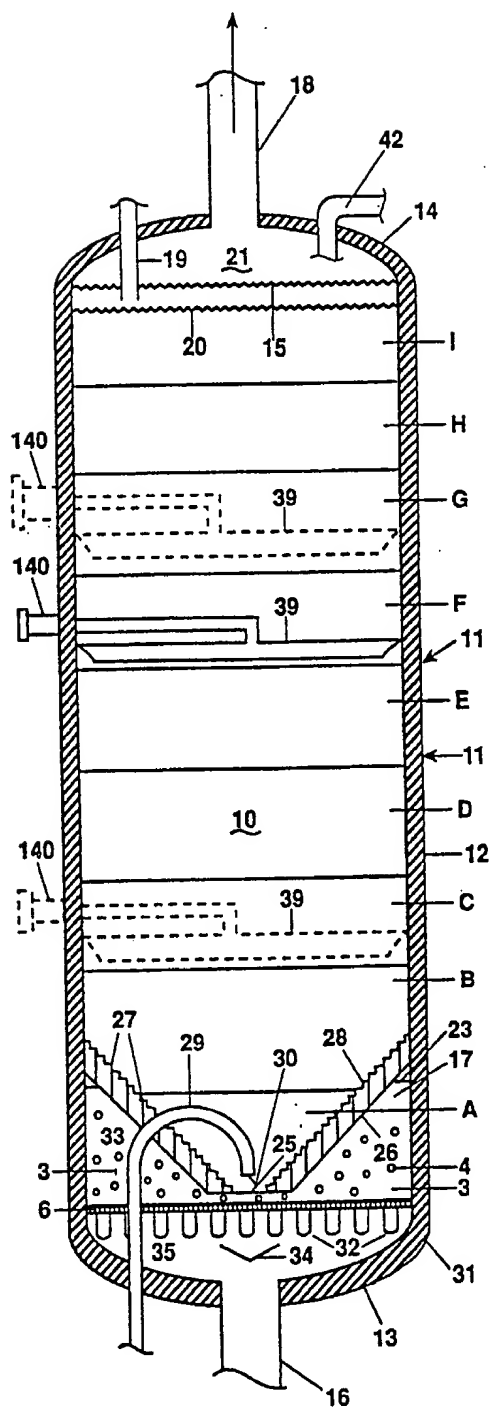


FIGURE 2

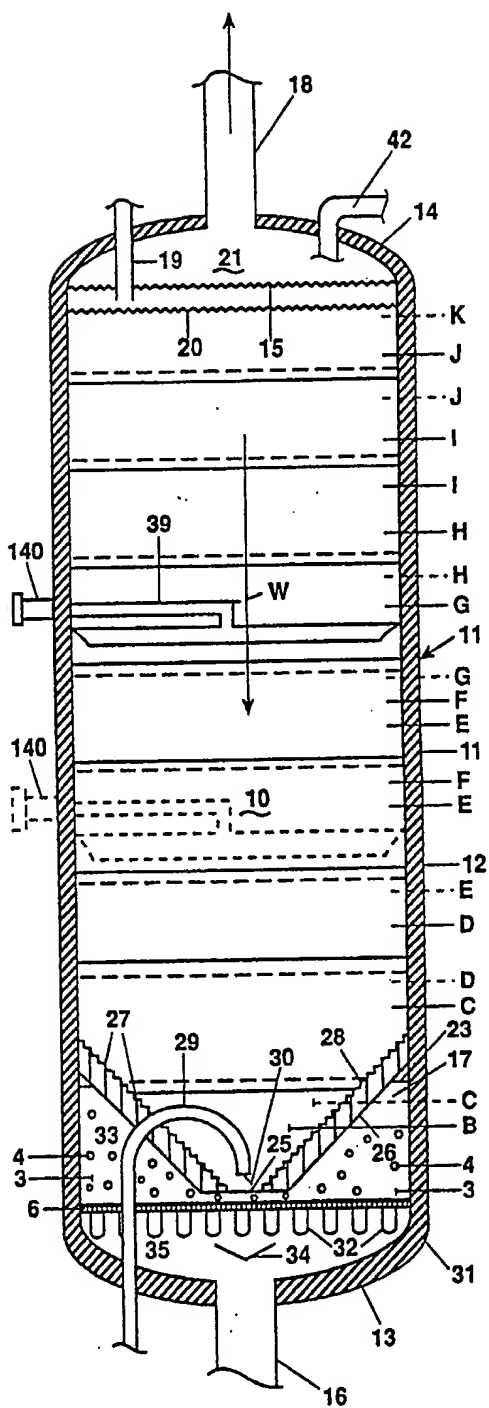


FIGURE 3

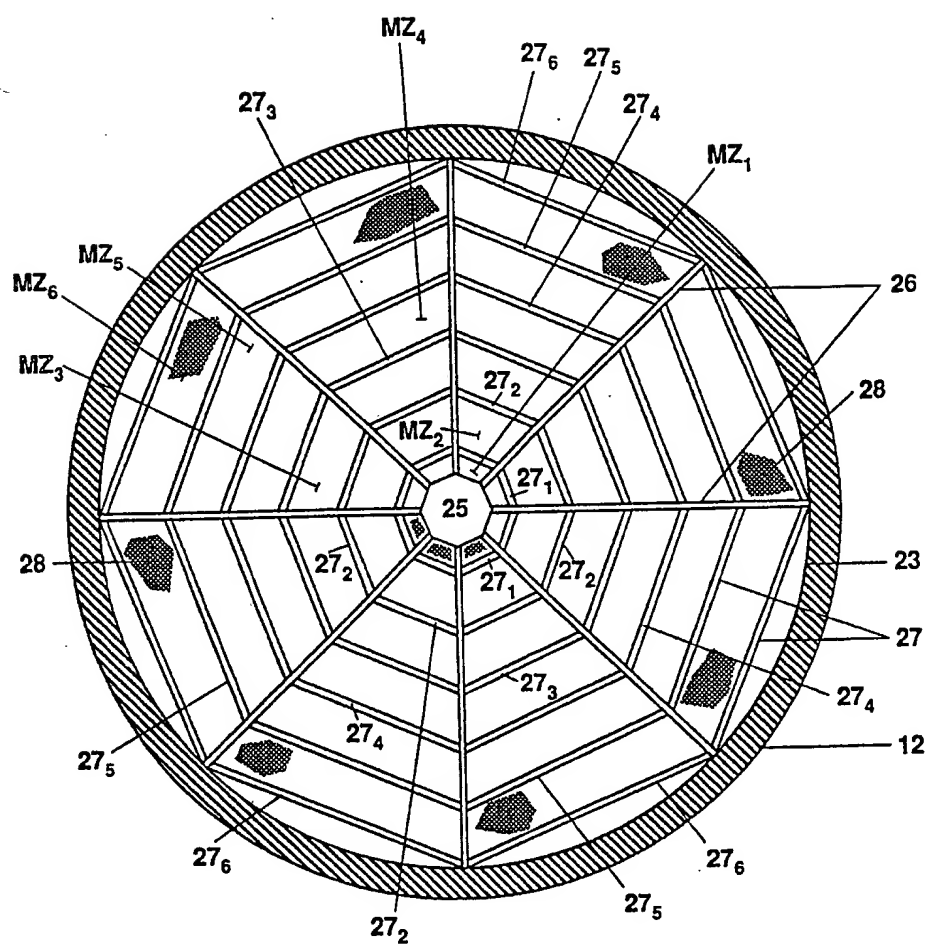


FIGURE 3A

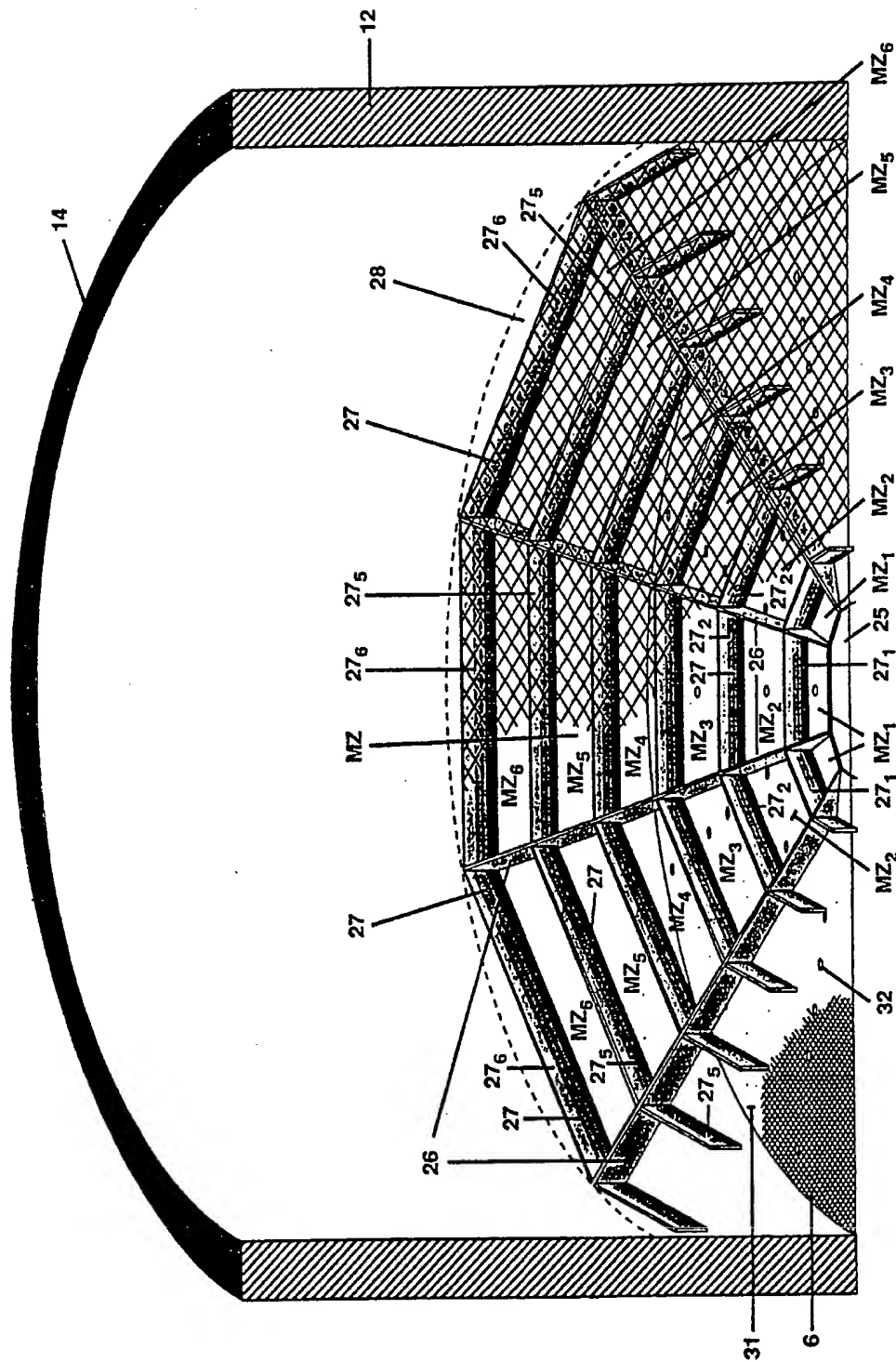


FIGURE 4

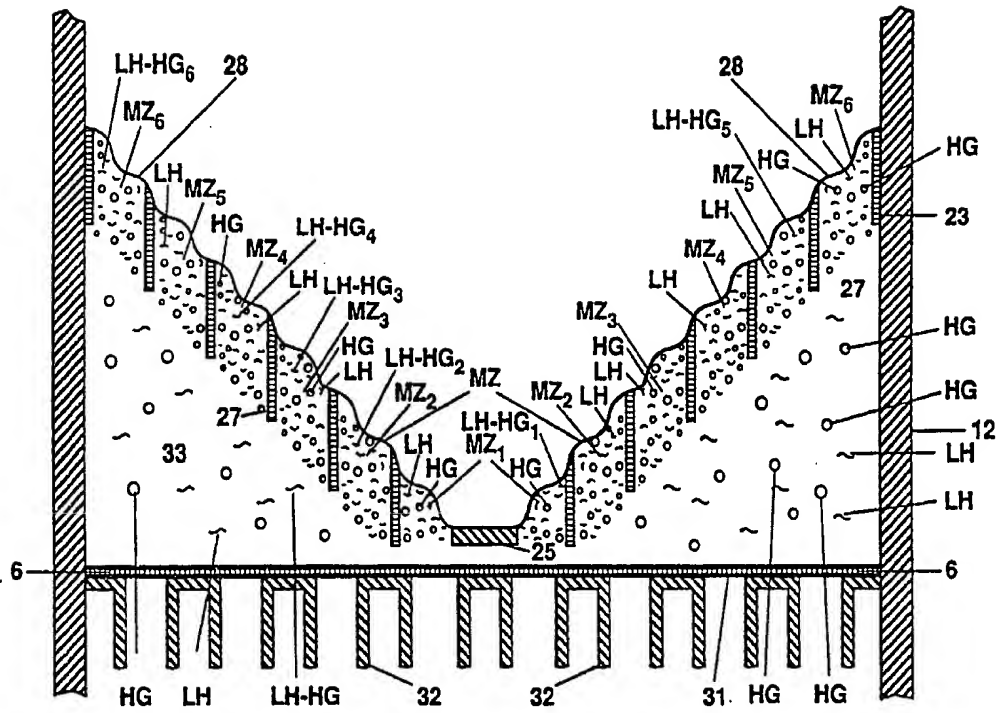


FIGURE 5

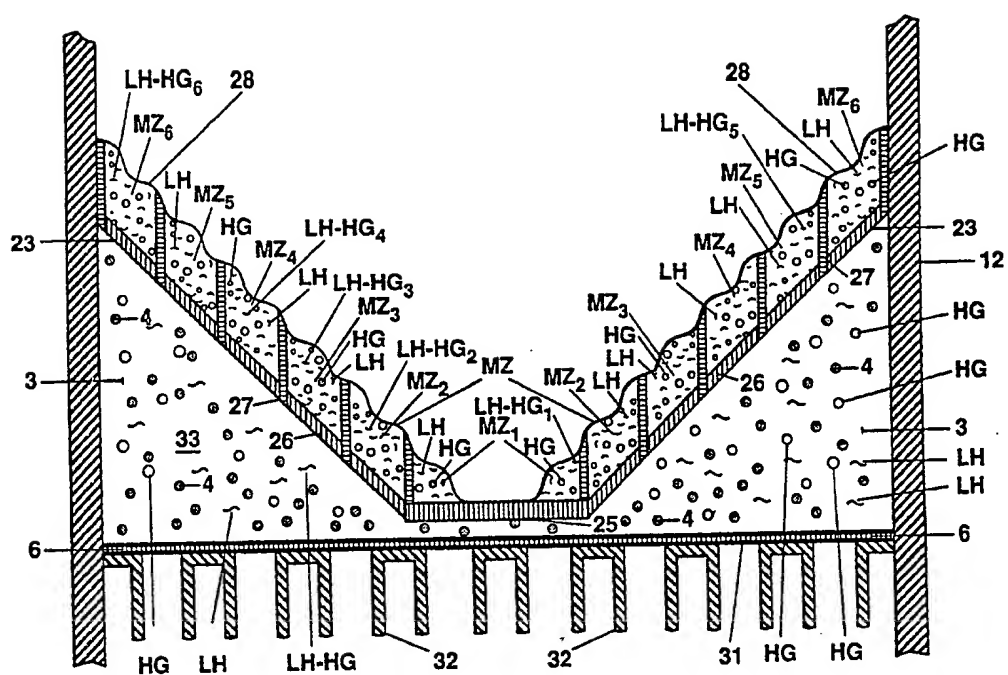


FIGURE 6

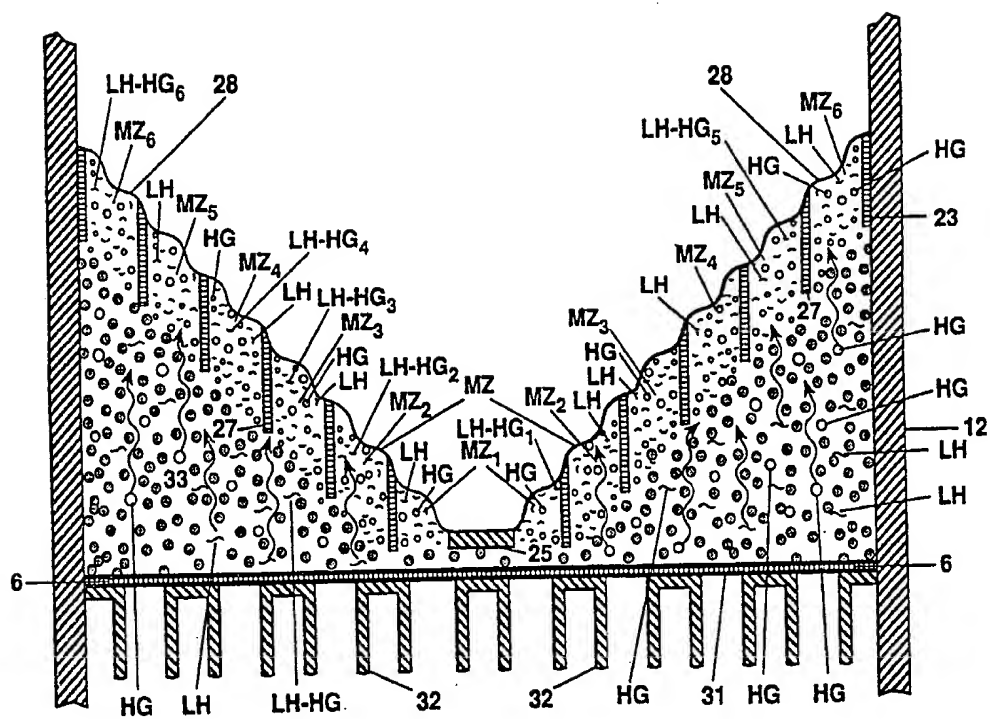


FIGURE 8A

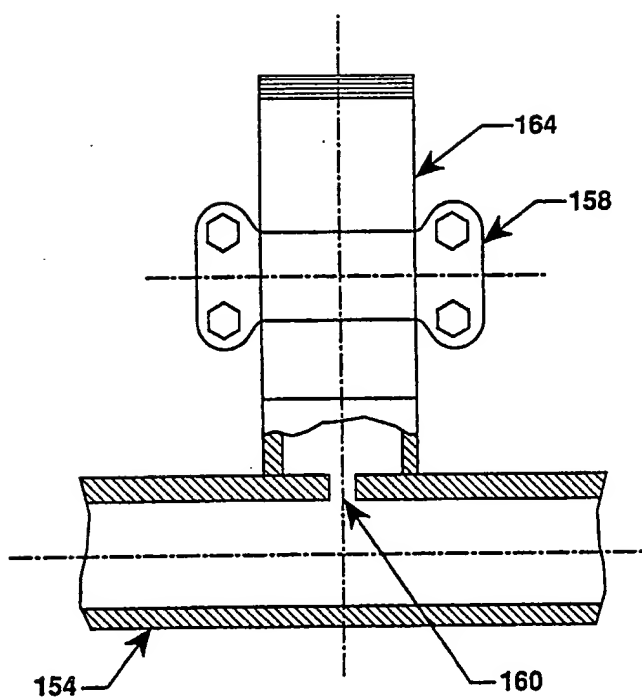


FIGURE 8

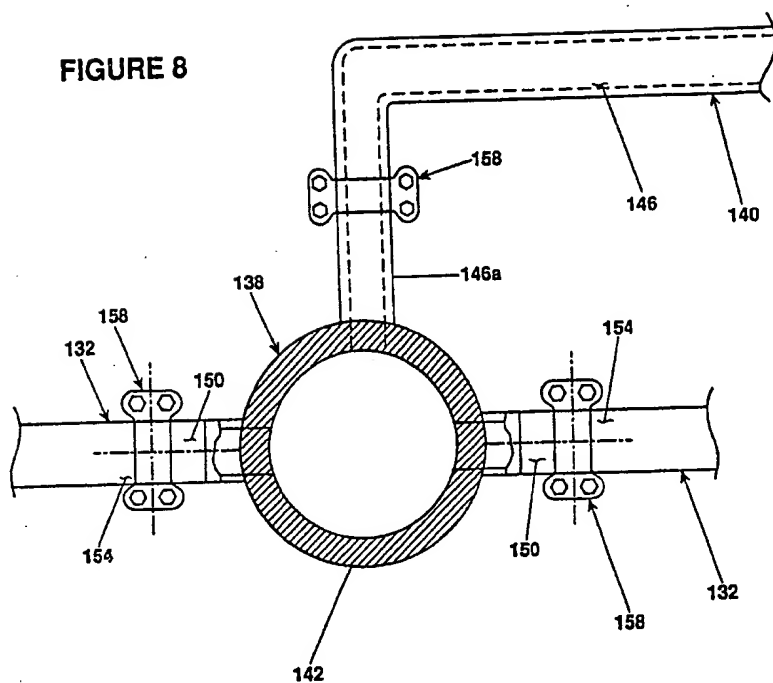
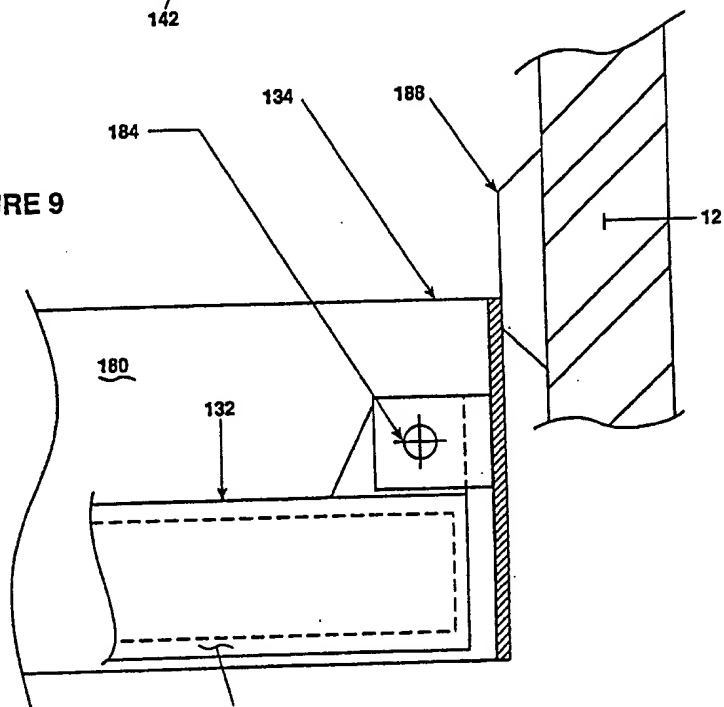
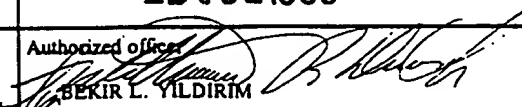


FIGURE 9



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/05280

A. CLASSIFICATION OF SUBJECT MATTER IPC(6) : C10G 11/18, 35/14 US CL : 208/146, 148, 157, 158, 165, 166 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 208/146, 148, 157, 158, 165, 166, 152,153 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) APS search terms:ebullated bed, size distribution, particle (size or diameter) bed expansion,		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y ---- A	US, A, 5,076,908 (STANGELAND ET AL) 31 December 1991, abstract, figures 2-3, cols. 7-8.	14-21 ----- 1-13
Y A	US, A, 3,887,455 (HAMNER ET AL) 03 JUNE 1975, abstract, col. 4, lines 20-60	14-21
A	US, A 5,302,357 (KRAMER ET AL) 12 APRIL 1994	1-21
A	US, A, 4,422,960 (SHIROTO ET AL) 27 December 1983	1-9
A, P	US, A, 5,409,598 (KRAMER ET AL) 25 April 1995	1-21
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* "A" "E" "L" "O" "P"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance earlier document published on or after the international filing date document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed	"T" "X" "Y" "&" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art document member of the same patent family
Date of the actual completion of the international search 16 JUNE 1995		Date of mailing of the international search report 12 JUL 1995
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer  BEKIR L. YILDIRIM Telephone No. (703) 308-3586